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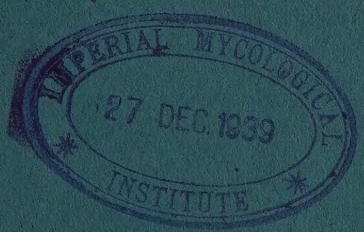

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TABLE DES MATIÈRES

MATHÉMATIQUES Pages

G. S. Chogoshvili (Г. С. Чогошвили). On Level Surfaces and Domains of Smaller Values of a Function Defined on a Bounded Manifold . . 635

B. Gnedenko (Б. Гнеденко). On the Domains of Attraction of Stable Laws 640

V. S. Lukchin (В. С. Люкшин). Invariabilité du nombre de fonctions arbitraires dépendant du plus grand nombre d'arguments dans le calcul inverse de la dérivation 643

V. Šmulian (В. Шмульян). On Some Geometrical Properties of the Sphere in a Space of the Type (B) 648

D. A. Raikov (Д. А. Райков). On the Local Approximation of Differentiable Functions 653

O. Volberg (О. А. Вольберг). Problème de la queue stationnaire et non-stationnaire 657

AÉRODYNAMIQUE

P. Elijasberg (П. Эльясберг). Sur la variation de la poussée d'une aile d'avion suivant la forme de son profil 662

PHYSIQUE

V. G. Chlopin (В. Г. Хлопин), Mitglied der Akademie, **M. A. Paswik-Chlopin (М. А. Пасвик-Хлопина)** und **N. F. Volkov (Н. Ф. Волков).** Über eine Art des Teilungsprozesses des Urankernes 665

A. Polessitsky (А. Полесицкий). Exchange of the Bromine Ions between AgBr and the Bromide Solution 668

N. Bautin (Н. Баутин). Du nombre de cycles limites naissant en cas de variation des coefficients d'un état d'équilibre du type foyer ou centre 669

A. Mayer (А. Майер). De trajectoires sur les surfaces orientées 673

V. I. Malyshev (В. И. Малышев). An Investigation of the Frequency of the O—H Group in Binary Mixtures by the Method of Combination Dispersion 676

Pages

G. A. Miljutin (Г. А. Милютин) and **S. S. Shalyt (С. С. Шалыт).** Magnetothermal Properties of Some Anomalous Paramagnetic Salts at Low Temperatures 680

M. L. Katz (М. Л. Кац) und **R. E. Ssolomoniuk (Р. Е. Соломонюк).** Ultraviolette Lumineszenz bei der Temperatur der flüssigen Luft röntgenisierten NaCl-Kristalle 683

I. L. Roich (И. Л. Ройх). Determination of the Sensitivity of a Photon Counter 687

P. A. Bajouline (П. А. Бажулин) et **J. M. Merson (Ю. М. Мерсон).** Absorption de sondes ultra-acoustiques dans un mélange acétone—eau 690

BIOPHYSIQUE

N. T. Fedorov (Н. Т. Федоров) and **V. I. Fedorova (В. И. Федорова).** Instantaneous Visual Threshold after Light Adaptation . . . 692

N. T. Fedorov (Н. Т. Федоров). Theory of the Eye's Photometric Sensitivity 696

N. T. Fedorov (Н. Т. Федоров) and **V. I. Fedorova (В. И. Федорова).** Photometric Sensitivity of the Eye 700

CHIMIE PHYSIQUE

E. S. Wasserman (Е. С. Вассерман). Chemiluminescence of 3-Amino-Phthalhydrazide (Luminol) 704

CHIMIE

I. N. Lepeshkov (И. Н. Лепешков) and **A. I. Shpikelman (А. И. Шпикельман).** Distribution of Boron between Liquid and Solid Phases of the Inder Lake Brines during Isothermal Evaporation 707

S. Z. Roginsky (С. З. Рогинский), Corresponding Member of the Academy, and **V. E. Tartakovskaja (В. Е. Тартаковская).** Investigation of Inter-Solvate Exchange of Bromine Ions in Various Solvents 709

AGROCHIMIE

I. V. Guliakin (И. В. Гулякин). Growth and Quality of Sugar-Beet Root as Influenced by Periodical Supply of Nitrogen and Potassium . 712

GÉNÉTIQUE

S. J. Krajevoj (С. Я. Краевой). On Natural Selection in Populations . 716

MORPHOLOGIE EXPÉRIMENTALE

V. V. Popov (В. В. Попов). On the Lens-Forming Ability of the Eye of Adult Amphibiae 720

PALÉONTOLOGIE

A. I. Argyropulo (А. И. Аргиропуло) and **I. G. Pidoplichka (И. Г. Пидопличка).** Representatives of *Ochotonidae (Duplicidentata, Mammalia)* in the Pliocene of the USSR 723

Rédacteur en chef A. Fersman. Rédacteur S. Bernstein.

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MATHEMATICS

ON LEVEL SURFACES AND DOMAINS OF SMALLER VALUES OF A FUNCTION DEFINED ON A BOUNDED MANIFOLD

By G. S. CHOGOSHVILI

(Communicated by A. N. Kolmogoroff, Member of the Academy, 1. VII. 1939)

Consider a bounded riemannian manifold R with the boundary B and a function f defined on it which induces on B the function f_b. R, B, f, f_b may satisfy the general boundary conditions ([2], [3], [4]). Previously ([4]) we have investigated the variations of the level surface and the domain of smaller values at the transition through a critical value of the function f. Now we shall investigate the same problems at a transition through a critical value of the function f_b.

There exist two kinds of critical points of the function f_b. At a critical point of the first kind the derivative in the direction normal to B at the point under consideration and pointing from the inside of the domain to the outside is positive; at a critical point of the second kind such a derivative is negative. Adopting this classification we prove the following theorems.

Theorem 1. *At the transition through a critical point of the first kind of the function f_b the Betti numbers of the domain of smaller values of the function f are not changed.*

At the transition through a critical point of the second kind of index k of the function f_b all Betti numbers of the domain of smaller values of the function f remain unchanged with the exception of the $(k-1)$-dimensional Betti number which (in this case) decreases by unity, or the k-dimensional which increases by unity.

Theorem 2. *At the transition through a critical point of index k of the function f_b all Betti numbers of the level surface of the function f remain unchanged with the exception of:*

In the case of the first kind: either the $(n-k-2)$-dimensional Betti number which increases by unity, or the $(n-k-1)$-dimensional which decreases by unity.

In the case of the second kind: either the $(k-1)$-dimensional which decreases by unity, or the k-dimensional which increases by unity.

Remark 1. In the proofs of both notes [of the present as well as of ([4])] it is assumed that to a critical value (of f_b or f) corresponds one critical point. But taking into account that at the transition through a critical point the variations occur only in an arbitrarily small neighbourhood of it, we may assume that to a critical value corresponds any finite number of critical points. In order to obtain the variations of the Betti numbers in this case we must algebraically add their variations corresponding to every critical point.

R e m a r k 2. Using the results of both notes and summing the variations of the Betti numbers of the domain of smaller values while the function increases from its absolute minimum to its absolute maximum, we obtain the known relations of Morse connecting the Betti numbers of the manifold with the numbers of critical points of the function [cf. (2), Theorem 10]. From the first part of Theorem 1 it becomes clear, why the critical points of the first kind are absent in these relations.

From the given definition of the kind of a critical point it is easy to pass to another definition which is more convenient for the proofs: at a critical point of the first kind and, consequently, at every point of its sufficiently small neighbourhood in B, the orthogonal trajectory of the function f passes out of the manifold R, i. e. terminates, whereas at a point of the second kind and at the points neighbouring to it this trajectory enters into the manifold, i. e. begins (when the parameter $t=f$ increases).

If p is a critical point of index k, $k \neq 0, n-1$, of the function f_b, then in a sufficiently small neighbourhood U of this point in B the function f_b may be represented up to infinitely small quantities of higher orders in the form $f_b = -x_1^2 - \ldots - x_k^2 + x_{k+1}^2 + \ldots + x_{n-1}^2 = -p_b^2 + q_b^2$.

Suppose first that p is a critical point of the first kind. We may choose numbers e and ε, $\varepsilon > e$, so small in modulus that $E[f_b \leqslant e^2, p_b^2 \leqslant \varepsilon^2] \subset U$.

In the first place to every level surface $f=c$, where $c_1 \leqslant c \leqslant c_2$ and c_1, c_2 satisfy the conditions $\varepsilon^2 < c_1 < 0$, $c_2 > 0$, the segment $[c_1, c_2]$ containing critical values neither of f, nor of f_b*, we must construct a border of breadth d_c along the part $E[f_b = c, p_b^2 \geqslant \varepsilon^2]$ of the boundary of this surface such that the arcs of this border starting at the points of $E[f_b = c, p_b^2 = \varepsilon^2]$ should form a border (of the same breadth d_c) of the set $E[f_b = c, p_b^2 \leqslant \varepsilon^2]$**.

To this end along that part of the boundary $f_b = c$ of the level surface $f=c$, where $p_b^2 \geqslant \varepsilon^2$, we construct a field of arcs, beling the intersections of planes normal to $f_b = c$ with $f=c$. It may be shown that these planes form a field in the neighbourhood of any point from $f_b = c$. The part of this field consisting of arcs beginning at the points of $E[f_b = c, \varepsilon_1^2 \geqslant p_b^2 \geqslant \varepsilon^2]$ may be continuously deformed in such a way that the arcs beginning at the points of $E[f_b = c, p_b^2 = \varepsilon_1^2]$ remain fixed and the arcs beginning at the points of $E[f_b = c, p_b^2 = \varepsilon^2]$ preserve their starting points and form at the end of the deformation a field in $E[f_b = c, p_b^2 \leqslant \varepsilon^2]$ (evidently along the boundary $E[f_b = c, p_b^2 = \varepsilon^2]$ of the last).

Among the positive numbers d_c, $c_1 \leqslant c \leqslant c_2$, there is a least, say, $d^* > 0$. If for all level surfaces we construct in this way a border of the breadth d^*, then in the domain $c_1 \leqslant f \leqslant c_2$ along that part of its boundary where $c_1 \leqslant f_b \leqslant c_2$, $p_b^2 \geqslant \varepsilon^2$ there arises a border of segments of the length d^* covering this border without intersections. The set of the end points of all segments evidently divides the domain into two parts.

On the level surface $f=c=0$ in its border just constructed take the set $[d]$ consisting of points chosen one on every arc, namely, points removed

---

* With the exception of the critical value 0, corresponding to the point p, of the function f_b.

** For those points, for which the assertion $p_b^2 \leqslant \varepsilon^2$ has no sense, i. e. which $\not\subset U$, this condition is taken to be satisfied.

from the beginning of the arc by d, $0<d<d^*$, where the distance is to be measured along the arc. The set $[d]$ is removed by a positive distance from the set of all end points of the arcs as well as from the set $B-E$ $[p_b^2<\varepsilon^2]$. Since both these sets are compact, the orthogonal trajectories $\{d\}$ and the level surfaces starting from points of $[d]$ may be continued to a sufficiently small distance in both directions such that none of them should go out of the constructed border at points of the mentioned sets, i. e. should meet neither $B-E$ $[p_b^2<\varepsilon^2]$, nor the end points. These trajectories so continued to a sufficiently small distance along decreasing $t=f$ will not go out of B at all (i. e. even at the points $p_b^2<\varepsilon^2$), since to go out along decreasing t means to go in along increasing t, which, according to the condition, cannot occur. In this direction they, consequently, reach the lower level surface. Continued along increasing t, some of them may go out; but they may go out, of course, only on the border of the set $p_b^2\leqslant\varepsilon^2$ and some trajectories may degenerate into points. The $(n-1)$-dimensional manifold $\{d\}$, if it is continued (in both directions) to a sufficiently short distance, will not meet any arc of our field more than once. The proof of this is based on the fact that any arc lying on the level surface sufficiently near to $f=c$ includes with $\{d\}$ an angle arbitrarily near to the right angle. Take now e^2 so small that the trajectories $\{d\}$ from $-e^2$ to e^2 should satisfy all the conditions stated above. In the direction of decreasing t the trajectories $\{d\}$ may not divide the domain, since the trajectories starting from points of $[d]$ lying on $f_b=0$ may enter into the domain. In this case take the set of end points of these last trajectories. It will represent the boundary of the intersection of $\{d\}$ with $f=-e^2$. Continue this intersection smoothly over this boundary to the boundary of $f=-e^2$ by means of an $(n-2)$-dimensional manifold lying in the constructed border of arcs of the level surface $f=-e^2$ and forming with the arcs angles exceeding a certain $\beta>0$. From this additional manifold let us issue orthogonal trajectories also in the direction of increasing t. They will smoothly join $\{d\}$, proceed inside the constructed border and go out of the domain before they reach $f=0$ (since otherwise they should be intersected by arcs more than once). The constructed trajectories separate the defined exterior part from the considered domain, since the manifold $\{d\}$ formed by them ($\{d\}$ denotes now and in the sequel all trajectories: those issuing from $[d]$, as well as those added to them) has the boundary lying on the boundary of the domain.

Take an arbitrary inner point of the domain $-e^2\leqslant f\leqslant e^2$, i. e. a point not lying between $\{d\}$ and B. This point cannot be a critical point of f, since there is no such in the domain $-e^2\leqslant f\leqslant e^2$. Consequently, through it passes an orthogonal trajectory which, continued along decreasing t, must reach an inner point of $f=-e^2$, since it can go out of this domain for decreasing t only at a point of $f=-e^2$ (it can meet for t decreasing neither $\{d\}$, nor $p_b^2\leqslant\varepsilon^2$, nor $f=-e^2$); continued along increasing t this trajectory either reaches $f=e^2$ (one of its inner points), or, before this (may be, from the outset, if the taken point lies on $p_b^2\leqslant\varepsilon^2$), it goes out of the domain at a point of the set $p_b^2\leqslant\varepsilon^2$ (also at an inner point of the same). The continuitability follows from the absence of critical points of f in this domain. Take now an arbitrary point of the exterior part. It lies on a certain arc of its level surface and divides it in a certain ratio l. Through the end of this arc passes a trajectory from $\{d\}$). Consider all arcs of our domain $-e^2\leqslant f\leqslant e^2$ terminating at the points of the trajectory under consideration. The set of points dividing them in the ratio l forms a line beginning in the exterior part of $f=-e^2$ and terminating in the exterior part of $f=e^2$ or $p_b^2\leqslant\varepsilon^2$. Consequently, the exterior part of the domain is exhausted by l-lines.

Thus, in the domain $-e^2 \leqq f \leqq e^2$ a field of lines is constructed which begin at the points of the surface $f = -e^2$ and terminate at the points of the manifold $E[f = e^2] + E[-e^2 \leqq f_b < e^2,\ p_b^2 \leqq \varepsilon^2]$.

For e_0 sufficiently near to e the domain $-e_0^2 \leqq f \leqq e^2$ may be filled [here already in the same way as in(4)] by lines which continue down the preceding. Once this being reached, we may establish by a well known method [the mapping of a point on a point of the same line dividing the new arc of the line in the same ratio, in which the original point divided the original arc, cf. (2, 4)] the following homeomorphisms.

1.1. The pre-critical domain of smaller values $f \leqq -e^2$ is homeomorphic to the after-critical domain $f \leqq e^2$.

1.2. The pre-critical level surface $f = -e^2$ is homeomorphic to the after-critical surface $f = e^2$ plus the manifold $E[-e^2 \leqq f_b \leqq e^2,\ p_b^2 \leqq \varepsilon^2]$.

A similar consideration of the case of a critical point of the second kind will show that:

2.1. The pre-critical domain of smaller values $f \leqq -e^2$ is homeomorphic to the after-critical domain $f \leqq e^2$, if we subtract from the latter the set of points lying on lines (orthogonal trajectories and l-lines) beginning at the points of the set $E[-e^2 \leqq f_b \leqq e^2,\ p_b^2 \leqq \varepsilon^2]$.

2.2. The after-critical level surface $f = e^2$ is homeomorphic to the beyond-critical surface $f = -e^2$ plus the manifold $E[-e^2 \leqq f_b \leqq e^2,\ p_b^2 \leqq \varepsilon^2]$.

From the thus established topological substance of the variation of the level surface corresponding to the domain of smaller values we shall deduce here the variations of the corresponding Betti numbers. The first part of Theorem 1 follows directly from 1.1. In order to obtain the second part we must investigate the influence of the subtraction involved in 2 : 1 on the Betti numbers *.

The set $D = E[-e^2 \leqq f_b \leqq e^2,\ p_b^2 \leqq \varepsilon^2]$ may be topologically mapped on the set $E[p_b^2 \leqq \varepsilon^2,\ q_b^2 \leqq \varepsilon^2 - e^2]$ such that points of D belonging to the surface $f = -e^2$ should be mapped on the set $E[p_b^2 = \varepsilon^2,\ q_b^2 = \varepsilon^2 - e^2]$.

The set D is, consequently, an $(n-1)$-dimensional cell and the set, which is obtained by restoration at the points of D of the l-lines and the orthogonal trajectories considered above, is topologically equivalent to the product of D and an one-dimensional cell. Denote this set by $\overline{D}$. D may be represented in the form of a topological product of a k-dimensional ball $\overline{a}_k$ (with the boundary S_{k-1}) and an $(n-k-1)$-dimensional ball $\overline{b}_{n-k-1}$ (with the boundary S_{n-k-2}). In this product that part of D which belongs to $f = -e^2$, i. e. the intersection $D[f = -e^2]$, is expressed as the product of the sphere S_{k-1} and the ball $\overline{b}_{n-k-1}$; whereas the part complementary to the preceding is given as the product of the interior of the ball $\overline{a}_k$ and the whole ball $\overline{b}_{n-k-1}$. Consequently, $\overline{D}$ may be given as the product of $\overline{a}_k$ and the $(n-k)$-dimensional ball $\overline{b}_{n-k}$ (with the boundary S_{n-k-1}) which is the product of the ball $\overline{b}_{n-k-1}$ and the one-dimensional ball.

From the above and from the fact that to the set $f \leqq -e^2$ (i. e. the set consisting of points belonging to the lines starting from the points

* All lines to be subtracted may be supposed to have a length > 0, since we may achieve this by constructing the border of the domain $-e^2 \leqq f \leqq e_0^2,\ e_0^2 > e^2$, i. e. already by consideration of the domain $f \leqq e_0^2$.

of the surface $f=-e^2$) may belong those and only those points of $\overline{D}$ which lie on the lines whose foot-points are points of the set $f_b=-e^2$, we conclude that the common part $\overline{D}\cdot\overline{f\leqslant -e^2}$ is the product of the sphere S_{k-1} and the ball $\overline{b}_{n-k}$; whereas the remaining part is representable as the product of $\overline{a}_k$ and $\overline{b}_{n-k}$.

The well known analysis of this circumstance ([1], [4]) leads to the second part of Theorem 1. In the same way from 1.2 and 2.2 we obtain Theorem 2. If the first part of this theorem is proved, the second part is more easily obtained by observing that the variation of the Betti numbers of the level surface of the function f at the transition through a critical point of the second kind of index k differs only in the sign from the variation of the Betti numbers of the level surface of the function $-f$ at the transition through a critical point of the first kind of index $n-k-1$; thus, the second part of Theorem 2 may be reduced to the first.

It remains to consider only the cases $k=0$ and $k=n-1$. Observe that the point of minimum of the function f_b ($k=0$) is a point of the first kind and the point of maximum ($k=n-1$) a point of the second kind. We shall assume that for $k=0$, f has no minimum, and for $k=n-1$, no maximum, not only relative, but even absolute.

Take such a neighbourhood U of the point p in R which induces in B a neighbourhood, in which the well-known representation of f_b holds. From this representation we see that in the case $k=n-1$, $E\,[-e^2\leqslant f_b\leqslant e^2]\;U$ is the $(n-1)$-dimensional ball. By a method already used the domain $-e^2\leqslant f\leqslant e^2$ for e sufficiently small (in particular, such that $f=-e^2$ and $f=e^2$ meet U) may be exhausted by l-lines and orthogonal trajectories issuing in the case $k=0$ from $f=-e^2$ and in the case $k=n-1$ from $E[f=-e^2]+E[-e^2{}_b\leqslant f_b\leqslant e^2]U$. For $k=0$, $f\leqslant -e^2$ and $f\leqslant e^2$ will be therefore homeomorphic. For $k=n-1$, $f\leqslant -e^2$ is obtained from $f\leqslant e^2$ topologically by removing the interior and the bases (but leaving the lateral surface) of the complete n-dimensional cylinder. The level surface $f=-e^2$ is obtained from $f=e^2$ by removing the interior of one $(n-1)$-dimensional cell for $k=n-1$ and by spanning a such for $k=0$. Hence we conclude about the variations of the Betti numbers in these cases.

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MATHEMATICS

ON THE DOMAINS OF ATTRACTION OF STABLE LAWS

By B. GNEDENKO

(Communicated by A. N. Kolmogoroff, Member of the Academy, 1.VII.1939)

It is said that the distribution law $F(x)$ belongs to the domain of attraction of the law $\Phi(x)$, if there exist such constants $B_n > 0$ and A_n that the distribution laws of the sums

$$S_n = \frac{x_1 + x_2 + \ldots + x_n}{B_n} - A_n \tag{1}$$

where $x_1, x_2, \ldots, x_n, \ldots$ are independent random variables distributed according to the law $F(x)$, converge to $\Phi(x)$.

It is known (1) that the class of limit laws in this sense coincides with the class of stable laws. In order that a law $\Phi(x)$ should be stable, it is necessary and sufficient (1) that the logarithm of its characteristical function $\varphi(t)$ should have the form

$$\lg \varphi(t) = i\gamma t - c_0 |t|^\alpha \left\{ 1 + i\beta \frac{t}{|t|} \omega(t, \alpha) \right\} \tag{2}$$

where α, β, γ, c_0 are constants ($0 \leqslant \alpha \leqslant 2$, $-2 \leqslant \beta \leqslant 1$, $-\infty < \gamma < +\infty$, $c_0 \geqslant 0$) and

$$\omega(t, \alpha) = \begin{cases} \operatorname{tg} \frac{\pi}{2} \alpha & \text{for } \alpha \neq 1 \\ \frac{2}{\pi} \lg |t| & \text{for } \alpha = 1. \end{cases}$$

At present there are known the domains of attraction of the Gauss' law ($\alpha = 2$) and the unit law ($\alpha = 0$)(1). Naturally enough, the fundamental problem of the theory of stable laws consists in determination of the domain of attraction for each of them.

The aim of the present note is to point out that the solution of this problem may be easily obtained by application of my general conditions of convergence of the distribution law of the sum of independent variables to some limit law(2). From the general theorem stated in my preceding note just referred to there follows

Theorem 1. *In order that for some sequence of natural numbers* K_n $(K_n \underset{n \to \infty}{\longrightarrow} \infty)$ *the distribution laws of the sums*

$$S'_n = \frac{x_1 + x_2 + \ldots + x_{n \cdot K_n}}{B'_n} - A'_n \tag{3}$$

where A'_n and B'_n are constants and $x_1, x_2, \ldots$ — independent random variables with one and the same distribution law $F(x)$, should converge to a limit law $\Phi(x)$, it is necessary and sufficient that there should exist functions $M(x)$ (for $-\infty < x < -0$) and $N(x)$ (for $+0 < x < +\infty$) and constants a and $\gamma(\tau)$ such that

$$K_n F(B'_n x) \underset{n\to\infty}{\longrightarrow} M(x) \text{ for } x < 0$$

1)

$$K_n [F(B'_n x) - 1] \underset{n\to\infty}{\longrightarrow} N(x) \text{ for } x > 0$$

and at every point of continuity of the functions $M(x)$ and $N(x)$

2) $$\lim_{\varepsilon\to 0} \lim_{n\to\infty} K_n \left\{ \int_{|x|<\varepsilon} x^2 \, dF(B'_n x) - \left(\int_{|x|<\varepsilon} x \, dF(B'_n x) \right)^2 \right\} = a^2$$

3) $$K_n \int_{|x|<\tau} x \, dF(B'_n x) - A'_n \underset{n\to\infty}{\longrightarrow} \gamma(\tau).$$

The logarithm of the characteristic function of the limit law is given by P. Lévy's formula:

$$\lg \varphi(t) = it\gamma(\tau) - \frac{a^2}{2} t^2 + \int_{-\infty}^{-\tau} (e^{itu} - 1) \, dM(u) + \int_{+\tau}^{\infty} (e^{itu} - 1) \, dN(u) +$$

$$+ \int_{-\tau}^{0} (e^{iut} - 1 - iut) \, dM(u) + \int_{0}^{\tau} (e^{iut} - 1 - iut) \, dN(u).$$

From Theorem 1 may be easily deduced the following theorem which was recently proved independently from my general results by W. Doeblin (3).

Theorem 2. *In order that the law $F(x)$ should belong to the domain of attraction of the stable law $\Phi(x)$, the logarithm of whose characteristic function is given by formula* (2) $(0 < \alpha < 2)$, *it is necessary and sufficient that the following conditions should be satisfied*:

1) $$\frac{F(-x)}{1 - F(x)} \underset{x\to+\infty}{\longrightarrow} c,$$

where c is a constant $(0 \leqslant c \leqslant +\infty)$,

2) *if* $0 < c < +\infty$, *then for any* $k > 0$

2a) $$\frac{F(-x)}{F(-kx)}_{x\to+\infty} \longrightarrow k^\alpha$$ *and* 2b) $$\frac{1 - F(x)}{1 - F(kx)}_{x\to+\infty} \longrightarrow k^\alpha;$$

in the cases $c = 0$ or $c = +\infty$ the conditions 2a) *or, respectively,* 2b) *must be omitted.*

If for $0 < x \leqslant 2$ the distribution law $F(x)$ coincides with the limit law $\Phi(x)$, then the constants B_n may be chosen equal to $n^{\frac{1}{\alpha}}$. In the case of an arbitrary law $F(x)$ it is therefore said that the law $F(x)$ belongs to the domain of normal attraction of the law $\Phi(x)$, if the constant coefficients B_n may be chosen equal to $an^{\frac{1}{\alpha}}$, where a is a constant. The question on the domains of normal attraction of stable laws is completely solved by the following theorem, which is also a consequence of Theorem 1.

Theorem 3. *In order that the distribution laws of the sums* (1) *should converge to a limit law, the logarithm of whose characteristic function is given by formula* (2) $(0 < \alpha < 2)$, *under the condition that the coefficients are chosen to be*

$$B_n = an^{\frac{1}{\alpha}},$$

where a is a constant, it is necessary and sufficient that the law $F(x)$ *should be representable in the form*

$$F(x) = [a_1 + \alpha_1(x)] \frac{1}{|x|^\alpha} \qquad \text{for } x < 0$$

$$F(x) = 1 - [a_2 + \alpha_2(x)] \frac{1}{x^\alpha} \qquad \text{for } x > 0$$

where a_1 *and* a_2 *are non-negative constants and the functions* $\alpha_1(x)$ *and* $\alpha_2(x)$ *satisfy the condition*

$$\lim_{x \to -\infty} \alpha_1(x) = \lim_{x \to +\infty} \alpha_2(x) = 0.$$

Let us in conclusion point out a property of Gauss' law which distinguishes it from other stable laws.

Theorem 4. *If the distribution laws of the sums* (3) *converge to Gauss' law for some sequence* K_n *and* $B_n = a\sqrt{K_n}$, *where a is a constant, then the distribution laws of the sums* (1) *converge also to Gauss' law, where we have to put* $B_n = a\sqrt{n}$.

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MATHÉMATIQUES

INVARIABILITÉ DU NOMBRE DE FONCTIONS ARBITRAIRES DÉPENDANT DU PLUS GRAND NOMBRE D'ARGUMENTS DANS LE CALCUL INVERSE DE LA DÉRIVATION

Par V. S. LUKCHIN

(Présenté par N. N. Lusin, de l'Académie, le 3.VII.1939)

Le calcul inverse de la dérivation consiste dans la résolution d'un système d'équations différentielles de la forme

$$\frac{\partial^{a_1+a_2+\ldots+a_n} u}{\partial x_1^{a_1} \partial x_2^{a_2} \ldots \partial x_n^{a_n}} = f_{a_1 a_2 \ldots a_n}(x_1, x_2, \ldots, x_n) \qquad (1)$$

le nombre de constantes et fonctions arbitraires devant être indiqué. u est la fonction cherchée, $f_{a_1 a_2 \ldots a_n}$ désigne les fonctions données de n variables indépendantes, supposées holomorphes au voisinage de $x_1 = x_2 = \ldots = x_n = 0$, par exemple.

Parmi les systèmes d'équations différentielles étudiées par Riquier, Janet(1) et Thomas(2) le système (1) est le plus simple. La méthode dont ils se servent est basée sur la théorie des monômes due à Riquier. La méthode exige d'ordonner les variables, et suivant cet ordre peut varier le nombre de constantes et de fonctions arbitraires dans la résolution du système (1).

Nous allons montrer que le nombre de fonctions arbitraires dépendant du plus grand nombre de variables indépendantes est invariant et ne dépend pas de la façon dont sont ordonnées les variables. Représentons la fonction cherchée par une série de Mac-Laurin

$$u = \sum_{i_1, i_2 \ldots i_n} a_{i_1, i_2 \ldots in} x_1^{i_1} x_2^{i_2} \ldots x_n^{i_n} \qquad (2)$$

convergente au voisinage de $x_1 = x_2 = \ldots = x_n = 0$.

Au lieu d'une dérivée quelconque $\frac{\partial^{i_1+i_2\ldots+i_n} u}{\partial x_1^{i_1} \partial x_2^{i_2} \ldots \partial x_n^{i_n}}$ on considère un produit symbolique $x_1^{i_1} x_2^{i_2} \ldots x_n^{i_n}$ qui lui correspond et que nous appelerons monôme. Les puissances $i_1, i_2, \ldots, i_n$ sont des entiers positifs ou nuls, $x_k^0 = 1$. A un système donné (1) d'équations différentielles correspond un système de monômes $M\{m\}$ $m = x_1^{a_1} x_2^{a_2} \ldots x_n^{a_n}$.

Désignons par j_k la plus grande des puissances x_k parmi les monômes du système donné M; appelons l'ensemble des nombres $j_1 j_2 \ldots j_n$

l'indice du système. Appelons de même x_k variable multiplicatrice du monôme m, s'il contient $x_k^{j_k}$, et variable non-multiplicatrice, si la puissance α_k de x_k sera $\alpha_k < j_k$.

Tous les multiples des monômes considérés s'obtiennent en multipliant des monômes du système M par leurs variables multiplicatrices ou bien non-multiplicatrices.

En multipliant m par des variables non-multiplicatrices et en multipliant les monômes ainsi obtenus par leurs variables non-multiplicatrices, nous obtenons un système complet des monômes M^* correspondant au système donné M et tel que la multiplication des monômes de M^* par des variables non-multiplicatrices ne nous fait pas sortir du système considéré. Le système complet M^*, dont l'indice est $j_1\, j_2 \ldots j_n$, contient le seul monôme $m^* = x^{j_1} x_2^{j_2} \ldots x_n^{j_n}$.

Sauf les monômes multiples des monômes M, il peut exister des monômes non-multiples des monômes M, qu'on appelle supplémentaires. Pour les former, il faut trouver tous les divisions m^* qui ne soient divisibles par aucun des monômes M. Désignons par $\overline{M}$ le système de monômes M supplémentaire. Il est évident que $\overline{M} + M^*$ contient tous les diviseurs m^*. Les systèmes $\overline{M}$ et M^* sont appelés (d'après Thomas), respectivement, système supplémentaire absolu et système complet.

La définition de la variable multiplicatrice ou bien non-multiplicatrice du monôme de M^* reste la même.

Soient deux monômes: $m = x_1^{\alpha_1} x_2^{\alpha_2} \ldots x_n^{\alpha_n}$ et $m' = x_1^{\beta_1} x_2^{\beta_2} \ldots x_n^{\beta_n}$; $m \neq m'$. Nous appelons m d'un rang absolu supérieur relativement à m', si aucune des différences $\alpha_1 - \beta_1$, $\alpha_2 - \beta_2, \ldots \alpha_n - \beta_n$ n'est négative.

La propriété des monômes $\overline{M} + M^*$ et de leurs multiples: *tout monôme est multiple du monôme unique de $\overline{M} + M^*$ d'un rang absolu le plus grand relativement aux monômes de $\overline{M} + M^*$ qui divisent le monôme considéré. Les multiples situés hors de $M + M^*$ s'obtiennent de cet unique monôme au moyen d'une multiplication par ses variables multiplicatrices.*

Appelons dans ce cas un tel monôme appartenant soit à M, soit à M^*, monôme générateur. On appelle classe l'ensemble de ses multiples obtenus en le multipliant rien que par ses variables multiplicatrices. Le nombre de ses variables est la mesure du monôme, ainsi que de la classe, à laquelle il donne naissance.

Tout l'ensemble de monômes multiples de $\overline{M} + M^*$ contient un nombre fini de classes non-superposables. Le nombre de tous les monômes compris en $\overline{M} + M^*$ est égal à $Q = (j_1 + 1)\ (j_2 + 1) \ldots (j_n + 1)$ tandis que le nombre de monômes générateurs est $Q = j_1 j_2 \ldots j_n$.

On peut maintenant représenter le développement (2) de la fonction u comme la somme d'un nombre fini Q de membres

$$u = \sum m_s F_s \qquad (3)$$

où m_s désigne un monôme $\overline{M} + M^*$, F_s—une fonction, lorsque m_s est un monôme générateur, les arguments de F_s étant les multiples de m_s; pour les monômes autres que le monôme générateur, F_s sont des constantes.

La fonction cherchée u est entièrement définie sans ambiguité par le théorème de Thomas (chap. XI) permettant de trouver toutes les F_s correspondant aux monômes m_s de M^*.

Le nombre de fonctions arbitraires dans la solution de u est égal au nombre de monômes générateurs du système absolu supplémentaire $\overline{M}$.

Le nombre d'arguments de ces fonctions arbitraires est déterminé par la mesure du monôme correspondant, et enfin, le nombre des constantes arbitraires est égal au nombre des monômes de $\overline{M}$, les monômes générateurs exceptés. Parmi les fonctions arbitraires il y a un certain nombre de fonctions dépendant du plus grand nombre d'arguments qui est toujours inférieur à n.

La théorie de Janet(1) est basée sur un autre procédé de formation de monômes qui exige d'ordonner les variables et de former les «systèmes complets». La fonction cherchée u est représentée par le développement (3) à un nombre de membres généralement plus petit, mais la définition de F_s reste exactement la même. Le nombre de ces membres dépend essentiellement de la façon d'ordonner les variables indépendantes.

Nous allons montrer: a) que le développement de Janet s'obtient de (3) de la même manière que Thomas obtient ses systèmes «relatifs» des systèmes absolus; b) que les définitions de Janet des variables multiplicatrices des monômes du système M ainsi que celles des monômes du système supplémentaire s'obtiennent sur la base de la même règle; c) que les monômes, donnant naissance aux classes infinies de Janet, sont de certains monômes générateurs, et d) que le nombre des monômes générateurs du système supplémentaire ayant le plus grand nombre de variables multiplicatrices reste invariant quelle que soit la façon d'ordonner les variables indépendantes.

Introduisons au lieu du monôme générateur m_s dans l'expression (3) un nouveau monôme m'_s tel que: 1) m'_s appartient à $\overline{M} + M^*$; 2) le rapport $m_s : m'_s$ ne contient que des variables multiplicatrices de m_s; 3) la substitution de m_s par m'_s se fait dans un ordre déterminé, par exemple d'après les indices de x croissants, c'est-à-dire en commençant par x_1, et enfin 4) attribuons à m'_s toutes les variables multiplicatrices de m_s. Alors tous les multiples de m'_s, obtenus au moyen d'une multiplication de m'_s par ses variables multiplicatrices, forment une nouvelle classe infinie comprenant l'ancienne classe correspondant au monôme m_s, et plusieurs monômes non-générateurs pour $\overline{M} + M^*$. Appelons m'_s nouveau monôme générateur et les systèmes obtenus de $\overline{M}$ et M^* — systèmes r e l a t i f s: $\overline{M}_{\text{rel}}$ et M^*_{rel}.

Lors d'un tel élargissement des classes les variables multiplicatrices des monômes, donnant naissance à ces classes, restent les mêmes que celles qui ont donné naissance aux classes primitives.

D'après Janet x_i sera la variable multiplicatrice de ceux des monômes, qui ont le même produit $x_n^{\alpha_n} x_{n-1}^{\alpha_{n-1}} \ldots x_{i+1}^{\alpha_{i+1}}$, x_i ayant la plus grande puissance α_i. En divisant tous les monômes en groupes ayant les mêmes $x_n^{\alpha_n} x_{n-1}^{\alpha_{n-1}} \ldots x_{i+1}^{\alpha_{i+1}}$, nous trouvons dans chacun des groupes le monôme avec le plus grand exposant des x_i. Soient $\alpha_i = \gamma_1, \gamma_2, \ldots \gamma_\lambda$ ces exposants. L'exposant le plus grand sera parmi les derniers, il est égal à j_i. Complétons maintenant le système donné des monômes par des multiples en multipliant par x_i, de manière à faire la puissance x_i^γ atteindre la valeur $x_i^{j_i}$. Les monômes obtenus auront x_i comme variable multiplicatrice dans le même sens que plus haut.

Le retour au système de monômes primitif s'effectue exactement d'après le procédé indiqué ci-dessus, car le rapport du monôme remplacé au monôme remplaçant contient $x_i^{j_i - \gamma}$, c'est-à-dire ne contient que la variable multiplicatrice du monôme remplaçant. Les monômes ayant x_i pour variables multiplicatrices d'après Janet seront d'après nous de nouveaux monômes générateurs. En refaisant le même raisonnement pour tous les x_i pris dans un ordre déterminé et en complétant le système primitif des monômes par les multiples au moyen de multiplica-

tion par des variables non-multiplicatrices des monômes et en raisonnant comme plus haut, nous trouverons que le système de monômes dont se sert Janet pour la résolution du système (1) n'est qu'un des systèmes relatifs M^*_{rel}.

On démontre de la même façon que les systèmes supplémentaires de Janet [(1) chap. I, p. 17] $N^{(n)}$, $N^{(n-1)},\ldots,N^{(1)}$ s'obtiennent de M et forment un système relatif supplémentaire $\overline{M}_{\text{rel}}$. Il suffit de démontrer pour cela que la définifion des variables multiplicatrices des monômes des systèmes de Janet N est la même que la définition des variables multiplicatrices des monômes du système M.

En effet, pour obtenir, par exemple, $N^{(n)}$ on considère tous les monômes x_n^β, où $\beta \geqslant 0$, $\beta < j_n$ et $\beta \neq \alpha_n$, c'est-à-dire où β n'est pas égal à aucune des puisances x_n des monômes du système M^*_{rel}. Alors $x_1, x_2, \ldots x_{n-1}$ sont, par définition, les variables multiplicatrices des monômes x_n^β. Il est évident que cette définition ne se distingue en rien de celle de la variable multiplicatrice du monôme M, car le monôme $x_n^\beta x_{n-1}^0$, par exemple, est unique: x_{n-1} est, par conséquent, la variable multiplicatrice du monôme x_n^β, etc.

En prenant maintenant le monôme $m = x_n^\beta x_{n-1}^{j_{n-1}} \ldots x_1^{j_1}$, nons voyons que le quotient $m : x_n^\beta$ ne contient que les variables multiplicatrices de m; pour cela x_n^β est un nouveau monôme générateur aux variables multiplicatrices $x_1, x_2, \ldots, x_{n-1}$. On obtient de la même manière tous les $N^{(i)}$ de Janet et nous voyons qu'ils forment un des systèmes relatifs supplémentaires $\overline{M}_{\text{rel}}$.

Pour un ordre déterminé des variables indépendantes formons un système de monômes N supplémentaire au «système complet». Il est le même qu'un certain système $\overline{M}_{\text{rel}}$. Tous les monômes générateurs de $\overline{M}_{\text{rel}}$ au moyen de leures variables multiplicatrices donnent naissance aux classes non-superposables des monômes qui ne sont pas multiples de M^*_{rel}.

Soit $\overline{m}'$ un certain monôme générateur de $\overline{M}_{\text{rel}}$ ayant un nombre de variables multiplicatrices le plus grand k. La multiplication par ces variables multiplicatrices nous donnera le monôme générateur m de $\overline{M}$, ayant le même nombre de variables multiplicatrices k. Il est évident que la classe a gardé sa mesure et reste due aux mêmes variables multiplicatrices. On obtiendra en même temps les monômes générateurs appartenant à $\overline{M}$, mais de mesure plus petite, car les monômes précédents $\overline{m}$ doivent le diviser et les variables multiplicatrices du numérateur $\overline{m}$, contenues dans le quotient, seront des variables non-multiplicatrices des diviseurs.

On obtiendra par là un système absolu supplémentaire $\overline{M}$ formé des monômes générateurs de $\overline{M}_{\text{rel}}$. Notons qu'on n'aura pas besoin d'une multiplication par des variables non-multiplicatrices, car ou bien nous passerons après une telle multiplication dans la classe suivante infinie, provenante d'un autre monôme générateur, ou bien nous obtiendrons un monôme ne faisant partie d'aucune classe infinie, mais appartenant au système supplémentaire. Un tel monôme n'est pas nouveau, car on l'avait obtenu en cours de formation de N. Ainsi, en passant de $\overline{M}_{\text{rel}}$ à $\overline{M}$ les variables multiplicatrices ne changent pas.

Supposons deux ordres distincts des arguments supplémentaires ayant μ et ν monômes, dépendant du plus grand nombre des variables multiplicatrices. Par le procédé indiqué plus haut nous obtiendrons de ces systèmes, des systèmes supplémentaires absolus. Ces derniers seront égaux et le nombre

de leurs monômes générateurs sera indépendant de la façon dont sont ordonnées les variables, car l'ordre des variables n'influait pas sur la formation de $\overline{M}$. Alors le nombre de monômes $\mu = \nu$, d'où le nombre des fonctions arbitraires dans le développement de u dépendant du plus grand nombre d'arguments, doit être constant pour le système donné[1].

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MATHEMATICS

ON SOME GEOMETRICAL PROPERTIES OF THE SPHERE IN A SPACE OF THE TYPE (B)

By V. ŠMULIAN

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Let E denote throughout the following a Banach space (1). A function $\|x\|$ is said to be weakly differentiable (2) at the point x_0, if there exists

$$\lim_{h\to 0} \frac{\|x_0+h\cdot x\|-\|x_0\|}{h} \qquad (x \in E) \qquad (1)$$

S. Mazur has shown (2) that weak differentiability of the norm $\|x\|$ at the point x_0 is equivalent to the existence of a single supporting hyperplane to the sphere $\|x\|\leqslant 1$ at the point x_0. If the convergence to the limit of the difference ratio $\frac{\|x_0+h\cdot x\|-\|x_0\|}{h}$ is uniform in the whole unit sphere $\|x\|\leqslant 1$, then $\|x\|$ is said to be strongly differentiable (2) at the point x_0.

Let Q be an arbitrary set. Then by $E(Q)$ we denote an arbitrary linear normed space of bounded functions defined in Q, where $|x| = \sup_{q\in Q} |x(q)|$.

The sequence of points $\{q_n\}\subset Q$ is called extremal for the function $x_0(q)\in E(Q)$, if there exists

$$\lim_{n\to\infty} x_0(q_n)$$

and

$$\|x_0\| = |\lim_{n\to\infty} x_0(q_n)|.$$

Lemma. *Let $x_0\in E(Q)$, $\|x_0\|=1$, and let $\{q_n\}\subset Q$ be an arbitrary extremal sequence of the function $x_0(q)$.*

Then for every element $x\in E(Q)$, $\|x\|\leqslant 1$, and for any number $0 \neq |h| \leqslant \frac{1}{4}$ there exists such a sequence $\left\{q_n^{(h;x)}\right\}\subset Q (n=1, 2,\ldots)$ that

$$\left.\begin{aligned} &\left|\frac{\|x_0+h\cdot x\|-\|x_0\|}{h} - \operatorname*{Lim}_{n\to\infty} x(q_n)\ \operatorname{sign}\lim_{n\to\infty} x_0(q_n)\right| \leqslant \\ &\leqslant \left|\operatorname*{Lim}_{n\to\infty} x(q_n)\ \operatorname{sign}\lim_{n\to\infty} x_0(q_n) - \lim_{n\to\infty} x(q_n^{(h;x)})\operatorname{sign}\lim_{n\to\infty} x_0(q_n^{(h;x)})\right| \end{aligned}\right\} \qquad (2)$$

Moreover,

$$\left|\ \left|\lim_{n\to\infty} x_0(q_n^{(h;x)})\right| - 1\ \right| \leqslant 2|h|. \qquad (3)$$

[Under the symbol Lim we understand here the generalized limit introduced by S. Banach (1)].

Proof. If $x \in E(Q)$, $\|x\| \leqslant 1$ and $0 \neq |h| \leqslant \frac{1}{4}$, then there exists such a sequence $\{q_n^{(h;x)}\} \subset Q$ that

$$\|x_0 + h\,x\| = \left| \lim_{n\to\infty} x_0(q_n^{(h;x)}) + h \cdot \lim_{n\to\infty} x(q_n^{(h;x)}) \right|.$$

Then

$$0 \leqslant \left| \lim_{n\to\infty} x_0(q_n) \right| - \left| \lim_{n\to\infty} x_0(q_n^{(h;x)}) \right| \leqslant \left| \operatorname*{Lim}_{n\to\infty} [x_0(q_n) + h \cdot x(q_n)] \right| +$$

$$+ |h| \cdot \left| \operatorname*{Lim}_{n\to\infty} x(q_n) \right| - \left| \lim_{n\to\infty} x_0(q_n^{(h;x)}) \right| \leqslant$$

$$\leqslant \left| \lim_{n\to\infty} x_0(q_n^{(h;x)}) + h \cdot \lim_{n\to\infty} x(q_n^{(h;x)}) \right| + \|x\| \cdot |h| - \left| \lim_{n\to\infty} x_0(q_n^{(h;x)}) \right| \leqslant$$

$$\leqslant |h| \cdot \|x\| + |h| \cdot \left| \lim_{n\to\infty} x(q_n^{(h;x)}) \right| \leqslant 2 \cdot |h| \cdot \|x\| \leqslant \cdot 2 \cdot |h|.$$

The inequality (3) is thus proved. We proceed now to prove the inequality (2). We have

$$\|x_0 + h \cdot x\| - \|x_0\| \geqslant \left| \lim_{n\to\infty} x_0(q_n) + h \cdot \operatorname*{Lim}_{n\to\infty} x(q^n) \right| - 1 =$$

$$= [1 + h \cdot \operatorname*{Lim}_{n\to\infty} x(q_n) \cdot \operatorname{sign} \lim_{n\to\infty} x_0(q_n)] - 1 = h \cdot \operatorname*{Lim}_{n\to\infty} x(q_n) \cdot \operatorname{sign} \lim_{n\to\infty} x_0(q_n).$$

On the other hand,

$$\|x_0 + h \cdot x\| - \|x_0\| = \left| \lim_{n\to\infty} x_0(q_n^{(h;x)}) + h \cdot \lim_{n\to\infty} x(q_n^{(h;x)}) \right] - 1 =$$

$$= \left[\left| \lim_{n\to\infty} x_0(q_n^{(h;x)}) \right| + h \cdot \lim_{n\to\infty} x(q_n^{(h;x)}) \cdot \operatorname{sign} \lim_{n\to\infty} x_0(q_n^{(h;x)}) \right] - 1 \leqslant$$

$$\leqslant h \cdot \lim_{n\to\infty} x(q_n^{(h;x)}) \cdot \operatorname{sign} \lim_{n\to\infty} x_0(q_n^{(h;x)})$$

For the proof of inequality (2) it remains only to compare the last two inequalities.

Theorem 1. *Let $x_0 \in E(Q)$, $\|x_0\| = 1$. Then for the strong differentiability of the norm $\|x\|$ in $E(Q)$ at the point x_0 it is sufficient that the following condition should be satisfied.*

For every extremal sequence $\{q_n\} \subset Q$ of the function $x_0(q)$ and every $x(q) \in (Q)$ $(\|x\| \leqslant 1)$ the sequence

$$\{x(q_n) \cdot x_0(q_n)\}$$

converges uniformly in the unit sphere $(\|x\| \leqslant 1)$ to a limit not depending on the choice of the extremal sequence $\{q_n\}$.

Proof. From the condition of the theorem follows that the right-hand side of the inequality (2) may be represented in the form

$$\left| \lim_{n\to\infty} [x(q_n) \cdot x_0(q_n)] - \lim_{n\to\infty} x(q_n^{(h;x)}) \cdot \operatorname{sign} \lim_{n\to\infty} x_0(q_n^{(h;x)}) \right|. \qquad (3)$$

In order to prove the theorem it is sufficient to show that the expression (3) tends to zero for $h \longrightarrow 0$ uniformly with respect to $\|x\| \leqslant 1$. Asssume, on the contrary, that there exists such an $\varepsilon_0 > 0$ that for every $0 < |h_p| \leqslant \frac{1}{2^{p+1}}$ $(p = 1, 2, \ldots)$ there may be found an $x_p \in E(Q)$, $\|x_p\| \leqslant 1$, for which

$$\left| \lim_{n\to\infty} [x_p(q_n) \cdot x_0(q_n)] - \lim_{n\to\infty} x_p(q_n^{(h_p;x_p)}) \cdot \operatorname{sign} \lim_{n\to\infty} x_0(q_n^{(h_p;x_p)}) \right| \geqslant \varepsilon_0 > 0. \quad (4)$$

Take such a sequence $\{n_p\}\to\infty$ that

$$\left| x_0(q_{n_p}^{(h_p;x_p)}) - \lim_{n\to\infty} x_0(q_n^{(h_p;x_p)}) \right| \leqslant \frac{1}{p} \quad (p=1,2,\ldots), \tag{5}$$

$$\left| x_p(q_{n_p}^{(h_p;x_p)}) - \lim_{n\to\infty} x_p(q_n^{(h_p;x_p)}) \right| \leqslant \frac{1}{p} \quad (p=1,2,\ldots). \tag{6}$$

Evidently, $\lim_{p\to\infty} |x_0(q_{n_p}^{(h_p;x_p)}| = 1$. We may suppose that $\lim_{p\to\infty} x_0(q_{n_p}^{(h_p;x_p)})$ exists and that, consequently, the sequence $\{q_{n_p}^{(h_p;x_p)}\}$ is extremal for the function $x_0(q)$. From the relations (4), (5) and (6) it follows that

$$\left| \lim_{n\to\infty}[x_p(q_n)\cdot x_0(q_n)] - x_p(q_{n_p}^{(h_p;x_p)})\cdot x_0(q_{n_p}^{(h_p;x_p)}) \right| \geqslant \frac{\varepsilon_0}{2}, \tag{7}$$

if p is sufficiently large. Since $\{q_n\}$ and $\{q_{n_p}^{(h_p;x_p)}\}$ are two extremal sequences for the function $x_0(q)$, from the condition of the theorem immediately follows the impossibility of the inequality (7) for arbitrarily large p. The theorem is thus proved.

Corollary 1. *If E is an arbitrary Banach space, then for strong differentiability of $\|f\|$ in $\bar{E}$ at the point f_0, $\|f_0\|=1$, it is sufficient that the following condition should be satisfied: from $f_0(x_n)\to\|f_0\|=1$, $\|x_n\|=1$ $(n=1,2,3,\ldots)$ follows that*

$$\|x_n - x_m\|\to 0 \quad \text{for } n,\ m\to\infty.$$

Corollary 2. *If E is an arbitrary Banach space, then for strong differentiability of $\|x\|$ in E at the point x_0, $\|x_0\|=1$, it is sufficient that the following condition should be satisfied: from $f_n(x_0)\to\|x_0\|=1$, $\|f_n\|=1$ $(n=1,2,3,\ldots)$ follows that*

$$\|f_n - f_m\|\to 0 \quad \text{for } n,m\to\infty.$$

Observe that Theorem 1 is a complement to my following theorem (7).

Theorem 2. *Let $x_0\in E(Q)$, $\|x_0\|=1$. Then for weak differentiability of the norm $\|x\|$ in $E(Q)$ at the point x_0 it is necessary and sufficient that the following condition should be satisfied: for every extremal sequence $\{q_n\}\subset Q$ of the function $x_0(q)$ and any $x(q)\in E(Q)$ the sequence*

$$\{x(q_n)\cdot x_0(q_n)\}$$

converges to a limit not depending on the choice of the extremal sequence $\{q_n\}$.

Corollary 1. *If E is a Banach space, then for weak differentiability of $\|f\|$ in $\bar{E}$ at the point f_0, $\|f_0\|=1$, it is necessary and sufficient that the following condition should be satisfied: if $f_0(x_n)\to 1$, $\|x_n\|=1$ $(n=1,2,\ldots)$, then the sequence $\{x_n\}$ converges weakly.*

Corollary 2. *If E is a Banach space, then for weak differentiability of $\|x\|$ in E at the point x_0, $\|x_0\|=1$, it is necessary and sufficient that the following condition should be satisfied: if $f_n(x_0)\to 1$, $\|f_n\|=1$, then*

$$\lim_{n\to\infty} f_n(x) \text{ exists for all } x\in E.$$

We shall say that the Banach space E is semi-uniformly convex, if from the relations

$$\|x_n\|=1,\ \lim_{n\to\infty}\left\|\frac{x_n+x_{n+k}}{2}\right\|=1 \tag{8}$$

(the convergence being uniform in $k=1,2,\ldots$) follows that

$$\|x_n - x_m\|\to 0 \quad \text{for } n,m\to\infty.$$

Every uniformly convex ([3]) space is semi-uniformly convex.

We shall say that the space E is weakly semi-uniformly convex, if from the relations (8) it follows that the sequence $\{x_n\}$ converges weakly to a certain element $x' \in E$. Every semi-uniformly convex space is weakly semi-uniformly convex.

Theorem 3. *If the space E is semi-uniformly convex, then $\|f\|$ is everywhere in $\bar{E}$ strongly differentiable.*

Proof. Let $\|f_0\|=1$, $f_0 \in \bar{E}$. Suppose that $f_0(x_n) \to 1$, $\|x_n\|=1$. We have to show that in this case $\|x_n - x_m\| \to 0$ for $n, m \to \infty$. In fact,

$$\|x_n\|+\|x_{n+k}\|=2 \leqslant f_0(x_n)+f_0(x_{n+k})+\varepsilon_n = f_0(x_n+x_{n+k})+ \\ +\varepsilon_n \leqslant \|x_n+x_{n+k}\|+\varepsilon_n \leqslant \|x_n\|+\|x_{n+k}\|+\varepsilon_n,$$

where $\lim_{n\to\infty} \varepsilon_n = 0$. Therefore the sequence $\{x_n\}$ satisfies the relations (8) and in virtue of the semi-uniform convexity of E the sequence $\{x_n\}$ converges. The theorem is proved.

Similarly we may prove the following proposition.

Theorem 4. *If the space E is weakly semi-uniformly convex, then $\|f\|$ is everywhere in $\bar{E}$ weakly differentiable.*

We have also the following

Theorem 5. *If the space E is uniformly convex, then from a) x_n converges weakly to x_0 and b) $\|x_n\| \to \|x_0\|$ follows $\|x_n - x_0\| \to 0$.*

D. Milman ([4]) has recently shown that a uniformly convex space is regular. From one result obtained by D. Milman in common with the author follows that a weakly semi-uniformly convex space is also regular.

S. Mazur ([5]) has proved the following proposition. Let: a) the unit sphere of E be weakly compact, b) the norm $\|x\|$ be everywhere strongly differentiable. Then:

1) For any bounded convex and closed set K and an arbitrary point $x_0 \in E$ lying outside K there exists always a closed sphere such that it contains the set K and does not contain the point x_0.

2) A sequence $\{x_n\}$ converges weakly to x_0 then and only then when it is bounded and every closed sphere containing infinitely many elements of $\{x_n\}$ contains also the point x_0, i. e.

3) A sequence $\{x_n\}$ converges weakly to x_0 then and only then when it is bounded and

$$\overline{\lim_{n\to\infty}} \|x_n - x\| \geqslant \|x_0 - x\| \quad (x \in E).$$

If the unit sphere *of* E is weakly compact and if the norm $\|x\|$ is everywhere in E weakly differentiable, then the space E is regular ([7]). Since, moreover, the unit sphere of a regular space is weakly compact ([6]), the spaces E possessing the properties a) and b) of S. Mazur's theorem referred to above coincide with regular spaces with strongly differentiable norm $\|x\|$.

From the preceding propositions easily follows that if the space E ($\bar{E}$) is semi-uniformly convex, then the space $\bar{E}$ (E) possesses the properties a) and b) of S. Mazur's theorem.

Theorem 6. *Let the space E satisfy the conditions a) and b) of S. Mazur's theorem and let $\{x_n\} \in E$, $\|x_n\|=1$, $(n=1, 2, \ldots)$. Then, in order that the point x_0 should possess the property:*

$$\overline{\lim_{n\to\infty}} f(x_n) \leqslant f(x_0) \leqslant \overline{\lim_{n\to\infty}} f(x_n) \quad (f \in \bar{E}),$$

it is necessary and sufficient that every closed sphere containing almost all $\{x_n\}$ should contain also the point x_0, i. e. that

$$\overline{\lim_{n\to\infty}} \| x_n - x \| \geqslant \| x_0 - x \| \quad (x \in E).$$

Theorem 7. *Let E and $\bar{E}$ be both uniformly convex. Then, in order that $\| x_n - x_0 \| \to 0$, it is necessary and sufficient that the following conditions should be satisfied:*

a) $\overline{\lim_{n\to\infty}} \| x_n - x \| \geqslant \| x_0 - x \| \quad (x \in E)$,

b) for some $x = x' \in E$
$$\lim_{n\to\infty} \| x_n - x' \| = \| x_0 - x' \|.$$

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MATHEMATICS

ON THE LOCAL APPROXIMATION OF DIFFERENTIABLE FUNCTIONS

By D. A. RAIKOV

(Communicated by A. N. Kolmogoroff, Member of the Academy, 30.VI.1939)

The principal aim of the present note is the proof of the following result establishing a connexion between the order of the local approximation of a function by polynomials of a given degree and its differential properties.

Theorem 1. *In order that a real function $f(x)$ should possess in the segment $[a, b]$ the n-th derivative satisfying the Lipschitz condition of the order $\alpha \leqslant 1$, it is necessary and sufficient that for all x_1, x_2 from $[a, b]$ the inequality $E_n[f(x); x_1, x_2] \leqslant C|x_1 - x_2|^{n+\alpha}$ should be satisfied, where C does not depend on x_1 and x_2, and $E_n[f(x); x_1, x_2]$ denotes the best approximation of the function $f(x)$ on the segment $[x_1, x_2]$ by a polynomial of the n-th degree.*

1. For the proof of necessity of the condition suppose that $|f^{(n)}(y) - f^{(n)}(x)| < C_1|y - x|^{\alpha}$ for all x, y from $[a, b]$, where C_1 does not depend on x and y. Put $\frac{x_1 + x_2}{2} = x_0$ and let $x \in [x_1, x_2]$. In virtue of Taylor's formula with the remainder in the integral form we have

$$f(x) = f(x_0) + f'(x_0)(x - x_0) + \ldots + \frac{f^{(n)}(x_0)}{n!}(x - x_0)^n + \\ + \frac{1}{(n-1)!}\int_{x_0}^{x}(x - y)^{n-1}[f^{(n)}(y) - f^{(n)}(x)]\,dy = P_n(x) + R_n(x)$$

and

$$E_n[f(x);\ x_1, x_2] \leqslant \max_{x \in [x_1, x_2]}|R_n(x)| < \frac{C_1}{(n-1)!}\int_{x_0}^{x}(x - y)^{n-1}(y - x_0)^{\alpha}\,dy = \\ = \frac{C_1\,\Gamma(1+\alpha)}{\Gamma(n+1+\alpha)}(x_2 - x_0)^{\alpha} = C(x_2 - x_1)^{n+\alpha}.$$

2. The proof of sufficiency is based on the following two lemmas.

Lemma 1. $|\Delta_h^{n+1} f(y)| \leqslant 2^{n+1} E_n[f(x); y, y + (n+1)h]$, *where $\Delta_h^{n+1} f(y)$ denotes the $(n+1)$-st difference with the step h of the function $f(x)$ at the point $x = y$.*

Lemma 2. *If $|\Delta_h^{n+1} f(x)| \leqslant C_1|h|^{n+\alpha}$ for all x and h such that $a \leqslant x$, $x + (n+1)h \leqslant b$, then $f(x)$ possesses in $[a, b]$ the n-th derivative satisfying the Lipschitz condition of the order α.*

The assertion of Lemma 2 is contained among the results of Marchaud (1). For the case $\alpha = 1$ we shall prove below [under the assumption of continuity of $f(x)$] a stronger result.

Proof of Lemma 1. As de la Vallée Poussin has shown (2)

$$E_n[f(x);\, c,\, d] = \max_{\substack{x_1, \ldots, x_{n+2} \in [c,\, d] \\ x_1 < \ldots < x_{n+2}}} \frac{\left| \sum_{i=1}^{n+2} (-1)^i f(x_i)\, W(x_1, \ldots, x_{i-1}, x_{i+1}, \ldots, x_{n+2}) \right|}{\sum_{i=1}^{n+2} W(x_1, \ldots, x_{i-1}, x_{i+1}, \ldots, x_{n+2})}, \quad (1)$$

where $W(x_1, \ldots, x_{i-1}, x_{i+1}, \ldots, x_{n+2})$ are Vandermonde's determinants. The formula (1) may be also written in the form

$$E_n[f(x);\, c,\, d] = \max \frac{|[x_1 \ldots x_{n+2}]_f|\, W(x_1, \ldots x_{i-1}, x_{i+1}, \ldots x_{n+2})}{\sum_{i=1}^{n+2} W(x_1, \ldots, x_{i-1}, x_{i+1}, \ldots, x_{n+2})}, \quad (2)$$

where $[x_1 \ldots x_{n+2}]_f$ denotes the $(n+1)$-st divided difference of the function $f(x)$ corresponding to the points $x_1, \ldots, x_{n+2}$*. Taking $c = y$, $x_i = y + (i-1)h$, $d = x_{n+2}$, we obtain

$$E_n[f(x);\, y,\, y+(n+1)h] \geqslant \frac{1}{(n+1)!} \left| \frac{\Delta_h^{n+1} f(y)}{h^{n+1}} \right| \frac{1!2! \ldots (n+1)!\, |h|^{\frac{(n+1)(n+2)}{2}}}{\sum_{k=0}^{n+1} \frac{1!2! \ldots (n+1)!}{k!\,(n+1-k)!} |h|^{\frac{n(n+1)}{2}}} =$$

$$= \frac{1}{2^{n+1}} \left| \Delta_h^{n+1} f(y) \right|,$$

wherefrom the assertion of Lemma 1 follows.

The sufficiency of the condition of Theorem 1 follows now immediately from Lemmas 1 and 2. In fact, let $E_n[f(x);\, x_1, x_2] < C\, |x_1 - x_2|^{n+\alpha}$ for all x_1, x_2 from $[a, b]$. Hence, in virtue of Lemma 1, we have

$$|\Delta_h^{n+1} f(y)| \leqslant 2^{n+1} E_n[f(x);\, y,\, y+(n+1)h] < C\, 2^{n+1} (n+1)^{n+\alpha} |h|^{n+\alpha}$$

and, consequently, in virtue of Lemma 2, $f(x)$ possesses in $[a, b]$ the n-th derivative satisfying the Lipschitz condition of the order α.

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* From formula (2) follows, by the way, directly that if for any set of $n+2$ points $x_1, \ldots, x_{n+2}$ of the segment $[a, b]$ the inequality $|[x_1 \ldots x_{n+2}]_f| < |[x_1 \ldots x_{n+2}]_g|$ is satisfied, then $E_n[f(x);\, a, b] < E_n[g(x);\, a, b]$. Hence we may easily deduce the following theorem of S. Bernstein (3): *If in* $[a, b]$ $|f^{(n+1)}(x)| < |g^{(n+1)}(x)|$, *then* $E_n[f(x);\, a, b] < E_n[g(x);\, a, b]$. To this end it is sufficient to observe that $\frac{[x_1 \ldots x_{n+2}]_f}{[x_1 \ldots x_{n+2}]_g} = \frac{f^{(n+1)}(\xi)}{g^{(n+1)}(\xi)}$, if only $f^{(n+1)}(x)$ and $g^{(n+1)}(x)$ do not vanish simultaneously [in our case $|g^{(n+1)}(x)| > 0$]. As to this (probably not new) generalization of Cauchy's formula, we consider for its proof the function

$$F(x) \equiv \begin{vmatrix} 1 & x_1 \ldots x_1^n & f(x_1) & g(x_1) \\ 1 & x_2 \ldots x_2^n & f(x_2) & g(x_2) \\ \cdot & \cdot \quad \cdot \quad \cdot & \cdot & \cdot \\ 1 & x_{n+2} \ldots x_{n+2}^n & f(x_{n+2}) & g(x_{n+2}) \\ 1 & x \ldots x^n & f(x) & g(x) \end{vmatrix}$$

and observe that it vanishes at $n+2$ points $x_1, \ldots, x_{n+2}$; therefore its $(n+1)$-st derivative vanishes at a certain intermediary point ξ and the assertion follows.

3. For $\alpha = 1$ and under the assumption of continuity of the function $f(x)$ Lemma 2 may be strengthened as follows.

Theorem 2. *If $f(x)$ is continuous in $[a, b]$ and there exists a sequence $h_k \to 0$ such that $|\Delta_{h_k}^{n+1} f(x)| < C|h_k|^{n+1}$ for all $x \in [a, b]$ and all $h^k, x+(n+1)h_k \in [a, b]$, where C does not depend on x and h_k, then $f(x)$ possesses in $[a, b]$ the n-th derivative satisfying the Lipschitz condition*

$$|f^{(n)}(x_2) - f^{(n)}(x_1)| \leqslant C|x_2 - x_1| \qquad (3)$$

for all $x_1, x_2 \in [a, b]$.

Proof. Put

$$f_h(x) = \frac{1}{h^{n+1}} \int_x^{x+h} dt_1 \int_{t_1}^{t_1+h} dt_2 \ldots \int_{t_n}^{t_n+h} f(t_{n+1})\, dt_{n+1};\ x,\ x+(n+1)h \in [a, b].$$

In virtue of the continuity of $f(x)$, $f_h(x) \to f(x)$ for $h \to 0$. Further, $f_h^{(n+1)}(x) = \frac{\Delta_h^{n+1} f(x)}{h^{n+1}}$. Thus, in virtue of the condition, $|f_{h_k}^{(n+1)}(x)| \leqslant C$ for all h_k and x, $x+(n+1)h_k \in [a, b]$. Hence it follows that the functions of the family $\{f_{h_k}^{(n)}(x)\}$ are equi-continuous, since

$$|f_{h_k}^{(n)}(x_2) - f_{h_k}^{(n)}(x_1)| = |f_{h_k}^{(n+1)}(\xi)(x_2 - x_1)| \leqslant C|x_2 - x_1|. \qquad (4)$$

Let us prove that they are also uniformly bounded. In fact, otherwise there would exist a sub-sequence h_{k_i} and a sequence of points $\xi_i \in [a, b]$ such that $|f_{h_{k_i}}^{(n)}(\xi_i)| \to \infty$. But then, in virtue of (4), the sequence $|f_{h_{k_i}}^{(n)}(x)|$ would uniformly tend to infinify and this is impossible, since $\Delta_h^n f_{h_{k_i}}(x) = f_{h_{k_i}}^{(n)}(\xi)\, h^n$ for a fixed h and $i \to \infty$ tends to $\Delta_h^n f(x)$, i. e. remains bounded.

From the equi-continuity and the uniform boundedness of the family $\{f_{h_k}^{(n)}(x)\}$ follows after Arzelà's theorem that we can choose from this family a uniformly convergent sub-sequence. But then the limit of this sub-sequence will be, as is known, the n-th derivative of $f(x)$. By a limiting process we obtain from (4) the Lipschitz condition (3) for $f^{(n)}(x)$.

S. Bernstein (4) has pointed out that if for an infinite set of values p and, for a fixed p, for an infinite sequence of values $h_{p,k} \to 0$ the inequality $|\Delta_{h_{p,k}}^p f(x)| < (R p h_{p,k})^p$, $R = \text{const}$, holds, then $f(x)$ is quasi-analytical (P) (with respect to the sequence of values p under consideration) *; in connexion with this he proposed the question: do all functions quasi-analytical (P) possess this property?

Theorem 2 enables us to deny this, since in virtue of this theorem the functions possessing the said property are indefinitely differentiable, whereas among the functions quasi-analytical in the sense of S. Bernstein there are non-differentiable functions.

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* The proof of this fact given in the Bernstein's monograph just referred to (p. 195) is based on the following generalization of Rolle's theorem: if $f(x)$ is a continuous function vanishing $n+1$ times in the segment $[a, b]$, then the equation $\Delta_h^n f(x) = 0$ possesses in $[a, b]$ at least one root for all sufficiently small h. The proof of this last proposition given by S. Bernstein is, however, as it may be easily remarked, insufficient.

In conclusion let us remark that for $\alpha < 1$ Lemma 2 cannot be strengthened in a similar way, i. e. the condition that $|\Delta_h^{n+1} f(x)| \leqslant C_1 |h|^{n+\alpha}$ should hold for a l l h cannot be replaced by the condition that this inequality should hold only for some arbitrary sequence $h_k \to 0$, as it has been done in Theorem 2 for the case $\alpha = 1$. In fact, as S. Bernstein has shown (5), there exist nowhere differentiable functions satisfying the last inequality (and even the stronger inequality $|\sup_{|h'| \leqslant h} \Delta_{h'}^{n+1} f(x)| \leqslant C_1 |h|^{n+\alpha}$) for any $\alpha < 1$ and some sequence $h = h_k \to 0$.

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MATHÉMATIQUES

PROBLÈME DE LA QUEUE STATIONNAIRE ET NON-STATIONNAIRE

Par O. VOLBERG

(Présenté par A. N. Kolmogoroff, de l'Académie, le 14.VI.1939)

Soit s le nombre de quelques appareils desservant un ensemble infini de clients qui peuvent exiger d'être desservis pendant l'un des deux intervalles de temps égaux avec la même probabilité. Nous considérons la moyenne fréquence α de demandes comme donnée.

Il est connu qu'en ce cas on peut considérer sous des conditions assez générales la probabilité de k demandes pendant un intervalle de temps t comme donnée par la loi de répartition de Poisson

$$v_k(t) = \frac{(\alpha t)^k}{k!} e^{-\alpha t} \qquad (1)$$

ce que nous allons admettre.

Ensuite nous allons considérer la fonction de répartition du temps de service $\psi(\mu)$ comme donnée

$$P(\mu_n^* \leqslant \mu) = \psi(\mu) \qquad (2)$$

où μ_n^* est la durée du service du $(n+1)$-ier client.

Nous allons établir avec F. Pollaczek[1] l'ordre d'utilisation des appareils suivant: chaque client qui exige d'être desservi, sera fixé à l'appareil dont c'est le tour, le client suivant—à l'appareil suivant, de sorte qu'ayant s appareils, chaque client remplace à l'appareil celui qui a demandé du service s hommes avant lui.

Nous admettons que le client, qui exige un service au moment où l'appareil est occupé, ne renonce à sa demande et se met en queue en attendant que l'appareil devienne vacant. Nous allons trouver la loi de répartition du temps d'attente du client qui exige d'être desservi au moment t.

Pour définir le problème il est nécessaire de donner les conditions initiales qui caractérisent le chargement initial des appareils. Désignons par $\pi_k(u)$ la probabilité pour que le temps u_k^* d'occupation initiale du $k+1$-ier appareil ne dépasse pas u:

$$\pi_k(u) = P(u_k^* \leqslant u) \quad (k = 0, 1, 2, \ldots s-1) \qquad (3)$$

et considérons les fonctions $\pi_k(u)$ $[0 \leqslant k \leqslant s-1]$ comme données.

Ensuite nous allons considérer les durées du service μ_n^* et d'occupation initiale u_k^* comme limitées du côté des grandes valeurs (et pas moins que 0), de sorte que nous supposerons les fonctions de répartition $\psi(\mu)$ et $\pi_k(u)$ $(k = 0, 1, \ldots s-1)$ égales à 1 pour les valeurs d'argument assez

grandes (et zéro pour les valeurs d'argument négatives, toujours monotones et continues du côté droit). Il nous est facile d'obtenir une formule récurrente qui résout notre problème.

Désignons par $\tau_n^*(t)$ le temps d'attente du $n+1$-ier client qui exige un service au moment t. Nous obtenons

$$\tau_{n+s}^*(t) = \overline{\tau_n^*(t - x_{n,s}^*) + \mu_n^* - x_{n,s}^*} \tag{4}$$

où $x_{n,s}^*$ est l'intervalle entre les demandes du $n+1$-ier et du $n+s+1$-ier client, dont le dernier exige un service au moment t. Nous désignons ici, comme ci-dessous, par une ligne au-dessus de la fonction qu'on la doit remplacer par 0 si l'argument est négatif.

Nous désignons encore que

$$\pi_n(\tau, t) = P[\tau_n^*(t) \leqslant \tau] \tag{5}$$

et

$$F_{n,s}(x, t) = P[x_{n,s}^* \leqslant x]. \tag{6}$$

Un calcul facile nous montre que

$$\frac{d}{dx} F_{n,s}(x, t) = \frac{\overline{(t-x)}^n}{n!} \cdot \frac{\overline{x}^{s-1}}{(s-1)!} \cdot \frac{(n+s)!}{t^{n+s}} \quad (t > 0) \tag{7}$$

Si nous prenons en considération (7), nous déduisons de (4) la formule récurrente cherchée:

$$\pi_{n+s}(\tau, t) \frac{\overline{t}^{n+s}}{(n+s)!} =$$

$$= \int_{-\infty}^{+\infty} d\psi(\mu) \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \overline{[\tau - (\tau' + \mu - x)]}^0 \, d_{\tau'} \, \pi_n(\tau', t-x) \cdot \frac{\overline{t-x}^n}{n!} \cdot \frac{\overline{x}^{s-1}}{(s-1)!} \, dx. \tag{8}$$

Cette formule* nous permet de trouver toutes les fonctions $\pi_n(\tau, t)$, si nous en savons les premières s fonctions, qui sont déterminées par les conditions initiales du problème:

$$\pi_n(\tau, t) = \overline{\tau}^0 \pi_n(\tau + t) \quad (n = 0, 1, \ldots s-1). \tag{9}$$

Pour trouver la loi de répartition $\pi(\tau, t)$ du temps d'attente du client dont nous ignorons complètement le numéro ordinal et qui exige d'être desservi au moment t, il faut remarquer que:

$$\pi(\tau, t) = \sum_{k=0}^{\infty} \pi_k(\tau, t) \, v_k(t) = e^{-\frac{t}{\lambda}} \sum_{k=0}^{\infty} \pi_k(\tau, t) \cdot \left(\frac{\overline{t}}{\lambda}\right)^k \cdot \frac{1}{k!} = \overline{e^{-\frac{t}{\lambda}}} \, A(\tau, t) \tag{10}$$

où $\lambda = \frac{1}{a}$ représente l'intervalle de temps moyen entre deux demandes du service successives.

De (8) nous trouvons, que la fonction $A(\tau, t)$ satisfait à l'équation intégrale

$$A(\tau, t) = H(\tau, t) +$$

$$+ \frac{1}{\lambda^s} \int_{-\infty}^{+\infty} d\psi(\mu) \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \overline{[\tau - (\tau' + \mu - x)]}^0 \, d_{\tau'} \, A(\tau', t-x) \, \frac{\overline{x}^{s-1}}{(s-1)!} \, dx \tag{11}$$

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* Le domaine d'intégration est déterminé par le facteur $\overline{[\tau - (\tau' + \mu - x)]}^0$, que nous considérons comme égal à 1, si $\tau \geqslant \tau' + \mu - x$, où zéro, si cette condition n'est pas remplie.

où

$$H(\tau, t) = \sum_{k=0}^{s-1} \pi_k(\tau, t) \cdot \left(\frac{\bar{t}}{\lambda}\right)^k \frac{1}{k!} = \bar{\tau}^0 \sum_{k=0}^{s-1} \pi_k(\tau + t) \left(\frac{\bar{t}}{\lambda}\right)^k \frac{1}{k!} \qquad (12)$$

Pour trouver la représentation asymptotique de la fonction $\pi(\tau, t)$ quand $t \to \infty$ nous allons nous baser sur cette équation. Nous désignerons

$$\int_0^\infty e^{-px}\, d\varphi(x) = \tilde{\varphi}(p) \qquad (13)$$

$$\int_0^\infty \int_0^\infty e^{-px-qy}\, d_x f(x, y) = \tilde{f}^*(p, q) \qquad (14)$$

et nous appelerons la fonction $\tilde{\varphi}(p)$ la caractéristique de Laplace-Stieltjes de la fonction $\varphi(x)$, et $\tilde{f}^*(p, q)$ la double caractéristique de Laplace de la fonction $f(x, y)$.

À l'aide de (11) nous trouvons

$$\tilde{A}^*(p, q) = \frac{\tilde{H}^*(p, q)(q-p)^s \lambda^s - pQ(p, q)}{(q-p)^s \lambda^s - \tilde{\psi}(p)} \qquad (15)$$

où $Q(p, q)$ est un polynôme de la $s-1$-ière puissance de la variable p, dont les coefficients dépendent de q et restent encore indéfinis. On peut les définir en considérant la régularité; notamment, on peut montrer que le dénominateur du côté droit de la formule (15) a s zéros $p_0^*(q)$, $p_1^*(q)$, , $\ldots$ $p_{s-1}^*(q)$ qui ont des parties positives réelles, si $R(q) > \frac{1}{\lambda}$. Puisque la fonction $\tilde{A}^*(p, q)$ doit être régulière quand $R(p) > 0$ et $R(q) > \frac{1}{\lambda}$, tous ces zéros du dénominateur doivent être en même temps les zéros du numérateur, de sorte que nous obtenons s valeurs du polynôme $Q(p, q)$ qui le déterminent complètement.

Ensuite nous désignerons par η le coefficient d'utilisation des appareils, c'est-à-dire le rapport du temps du service moyen μ_1 à $s\lambda$: $\eta = \frac{\mu_1}{s\lambda}$.

On peut montrer qu'une fonction entière symétrique des zéros $p_0^*(q)$, $p_1^*(q)$, $\ldots$ $p_{s-1}^*(q)$ du dénominateur de la fonction $\tilde{A}^*(p, q)$ est régulière quand $R(q) > \frac{1}{\lambda}$ ou même dans un domaine plus vaste $R(q) > a$, si le coefficient d'utilisation η n'est pas 1 $\left(a \text{ est un nombre} < \frac{1}{\lambda}\right)$. Si nous prenons en considération qu'avec $\eta < 1$ les zéros du dénominateur de la fonction $\tilde{A}^*(p, q)$ [c.-à-d. les fonctions $p_k^*(q)$] possèdent des zéros aux points $q = q_k = \frac{1}{\lambda}\zeta_k$, où $\zeta_k = e^{\frac{2k\pi i}{s}}$, tandis qu'avec $\eta > 1$ les zéros du dénominateur n'ont pas de zéros, nous obtenons le résultat que si $\eta < 1$, la fonction $\tilde{A}^*$ a dans le plan q la singularité extrême droite au point $q = q_0 = \frac{1}{\lambda}$ (pôle simple).

Il nous est facile de calculer le résidu de la fonction $\tilde{A}^*$ par rapport à ce pôle et de trouver une telle représentation de cette fonction

$$\tilde{A}^*(p, q) = \frac{pQ(p)}{\tilde{\psi}(p) - (1 - \lambda p)^s} \cdot \frac{1}{q - \frac{1}{\lambda}} + \tilde{\varphi}^*(p, q) \quad (\eta < 1) \qquad (16)$$

où la fonction $\tilde{\varphi}^*$ est régulière quand $R(p) > 0$ et $R(q) > a$ $\left(a \text{ est un peu moins que } \frac{1}{\lambda}\right)$ et $Q(p)$ est un polynôme, dont les zéros coïncident avec les zéros du dénominateur, situés dans le demi-plan droit. Si p devient 0, ce polynôme se transforme en $s\lambda(1-\eta)$, c.-à.-d.

$$Q(p) = \frac{s\lambda(1-\eta)(p_1-p)(p_2-p)\cdots(p_{s-1}-p)}{p_1 p_2 \cdots p_{s-1}} \tag{17}$$

(p_k sont les zéros de la fonction $\tilde{\psi}(p) - (1-\lambda p)^s$, situés dans le demi-plan droit).

Nous allons faire usage d'un lemme afin d'obtenir la représentation asymptotique de la fonction $\tilde{\pi}(p, t)$ quand $t \to \infty$.

Lemme. Si la fonction $\varphi(q)$ est régulière quand $R(q) > a$ et tend vers 0 uniformément par rapport à arg q quand $q \to \infty$, s'il est possible de la représenter sur la droite $R(q) = a' > a$ en forme de $\varphi(q) = \frac{c}{q^\alpha} + O\left(\frac{1}{q^{1+\beta}}\right)$ [$q \to \infty$, $c = \text{const}$, $\alpha > 0$, $\beta > 0$], c'est alors que cette fonction est la caractéristique de Laplace de la fonction $\Phi(t)$. Cette dernière croît quand $t \to \infty$ plus lentement que la fonction $e^{a't}$, c.-à.-d.

$$\varphi(q) = \int_0^\infty e^{-qt}\Phi(t)\,dt$$

et

$$\lim_{t\to\infty}[\Phi(t)\,e^{-a't}] = 0.$$

A l'aide de ce lemme, qui se laisse déduire presque immédiatement des études de Haar [2] sur des représentations asymptotiques des fonctions, nous obtenons

$$\tilde{\pi}(p, t) = \frac{pQ(p)}{\tilde{\psi}(p) - (1-\lambda p)^s}\left[1 + O(e^{-\rho' t})\right] \tag{18}$$

où $\rho > \rho' > 0$ (ρ' est indépendant de p).

De cette manière si le coefficient d'utilisation des appareils $\eta < 1$, *la fonction de répartition du temps d'attente du client qui demande d'être desservi au moment t tend (quand $t \to \infty$) vers une loi stationnaire $\pi(\tau)$; cette dernière ne dépend pas du temps et sa fonction caractéristique est égale à*

$$\tilde{\pi}(p) = \frac{pQ(p)}{\tilde{\psi}(p) - (1-\lambda p)^s}. \tag{19}$$

Dans le cas où $s = 1$, la fonction caractéristique a été trouvée par A. Khintchine [3].

Quand $\eta > 1$ les zéros de la fonction $\tilde{A}^*$ n'ont pas de zéros comme nous l'avons déjà dit. En ce cas nous avons pour les valeurs de p voisines à 0 et situées dans le demi-plan $R(p) > 0$ le point $q = q_0(p) = p + \frac{1}{\lambda}[\tilde{\psi}(p)]^{\frac{1}{s}}$ pour singularité droite extrême (pôle simple) de la fonction $\tilde{A}^*$.

La fonction $\tilde{A}^*(p, q)$ se laisse écrire pour les valeurs de p voisines à 0 et situées dans le demi-plan $R(p) > 0$ de la façon suivante:

$$\tilde{A}^*(p, q) = \left[\tilde{H}^*(p, q) - \frac{pQ(p, q_0)}{\tilde{\psi}(p)}\right] \cdot \frac{q_0 - p}{s} \cdot \frac{1}{q - q_0} + \tilde{\varphi}_1^*(p, q)$$

où $q_0 = p + \frac{1}{\lambda}[\tilde{\psi}(p)]^{\frac{1}{s}}$ et $\tilde{\varphi}_1^*(p, q)$ est une fonction régulière dans le demi-plan $R(q) > a$, où a est un peu moins que $\frac{1}{\lambda}$. Nous trouvons à l'aide du lemme précité (si p est voisin à 0 et situé dans le demi-plan droit):

$$\tilde{\pi}(p, t) = \left[\tilde{H}^*(p, q_0) - \frac{pQ(p, q_0)}{\tilde{\psi}(p)}\right]\frac{q_0 - p}{s} e^{-\left(\frac{1}{\lambda} - q_0\right)t}[1 + O(e^{-\rho' t})] \qquad (20)$$

où $\rho > \rho' > 0$ (et ρ' est indépendant de p).

Il nous est maintenant facile d'obtenir

$$\lim_{t\to\infty} P\left[\frac{\tau^*(t) - (\eta - 1)t}{\sqrt{\frac{t}{\lambda}}} \leqslant \tau\right] = \lim_{t\to\infty} \pi\left[\sqrt{\frac{t}{\lambda}} \cdot \tau + (\eta - 1)t, t\right].$$

La substitution de l'argument τ par $\sqrt{\frac{t}{\lambda}}\,\tau + (\eta - 1)t$ dans la fonction de répartition a comme conséquence la substitution de p par $p\sqrt{\frac{\lambda}{t}}$ dans sa caractéristique de Laplace-Stieltjes et la multiplication de cette dernière par $e^{\sqrt{\lambda t}(\eta-1)p}$. Après avoir executé cette substitution dans (20) nous obtenons

$$\lim_{t\to\infty} \tilde{\pi}\left(p\sqrt{\frac{\lambda}{t}}, t\right) e^{\sqrt{\lambda t}(\eta-1)p} = e^{\left[\frac{\mu_2 - \mu_1^2}{s} + \frac{\mu_1^2}{s^2}\right]\frac{p^2}{2}} \qquad (21)$$

où nous désignons par μ_2 le second moment de la fonction de répartition du temps de service.

Il en résulte que

$$\lim_{t\to\infty} \pi\left(\sqrt{\frac{t}{\lambda}} \cdot \tau + (\eta - 1)t, t\right) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\tau\sqrt{\frac{\mu_2 - \mu_1^2}{s} + \frac{\mu_1^2}{s^2}}} e^{-\frac{x^2}{2}} dx,$$

c.-à.-d. que (quand $\eta > 1$) les durées d'attente, normées de la manière susdite, suivent, quand $t \to \infty$, la loi normale limite de répartition de Gauss.

Dans un autre article[4], j'ai étudié le problème de répartition du temps d'attente du client, dont le numéro ordinal croît infiniment, et j'ai obtenu des résultats analogues; seulement la dispersion de la loi limite de répartition a été un peu plus petite.

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AÉRODYNAMIQUE

SUR LA VARIATION DE LA POUSSÉE D'UNE AILE D'AVION SUIVANT LA FORME DE SON PROFIL

Par P. ELIJASBERG

(Présenté par N. E. Kotchine, de l'Académie, le 22. VI. 1939)

Soit donné un arc convexe simple $C : AB$ formant dans le point A l'angle τ avec le sens négatif de l'axe OX. La courbure de l'arc est inférieure à un nombre k et la longueur de sa corde est égale à l. Supposons que l'arc C soit placé dans le courant d'un fluide idéal incompressible en translation, dont la vitesse à l'infini est parallèle à l'axe OX et pour lequel le point A est un point de convergence. Soit $P(C)$ la poussée de l'arc C causée par le courant donné.

Théorème I. *Ils existent des constantes m et τ_0 telles que parmi tous les arcs convexes possédant les propriétés indiquées ci-dessus, à savoir, formant les angles aigus avec la corde AB et pour lesquels $k < \frac{m}{l}$, $\tau < \tau_0$, le segment rectiligne de longueur l donne la poussée $P(C)$ la plus grande. On peut prendre $m = \frac{1}{4}$; $\tau_0 = 30°$.*

Observons qu'en précisant le calcul au cours de la démonstration on peut augmenter les valeurs des constantes m et τ. Or, en se servant des mêmes méthodes, on peut montré que pour une croissance illimitée de la constante m la valeur maximum de la constante τ_0 tend vers zéro.

Indiquons la marche de la démonstration.

Soit $\zeta = f(z, C)$ la fonction représentant l'extérieur de l'arc C sur l'extérieur du cercle $|\zeta| > 1$ à condition que

$$f(\infty, C) = \infty, \quad \arg f'(\infty, C) = 0.$$

Sans diminuer la généralité, on peut supposer la corde de l'arc C égale à 4. Alors il est facile de montrer, en se servant de la formule de Joukovsky, que la démonstration du théorème I se réduit à la démonstration de l'inégalité

$$\sin \tau > \frac{\sin \varphi [C; A]}{f'(\infty, C)} \tag{1}$$

où

$$\varphi [C; A] = -\arg f(A; C).$$

La question se réduit donc à la recherche des valeurs correspondantes des fonctionnables $\varphi [C; A]$ et $f'(\infty, C)$. Il est facile de trouver ces valeurs au moyen des théorèmes suivants.

Théorème II. *Soient donnés deux arcs simples convexes C et C' ayant les mêmes extrémités A et B. L'arc C' est de plus situé du côté convexe de l'arc C. Alors on a*

$$f'(\infty, C') < f'(\infty, C). \tag{2}$$

Il est évident que pour démontrer le théorème dans le cas général, il suffit de le prouver dans le cas des arcs analytiques infiniment voisins (au point de vue de la distance aussi bien que de l'inclinaison de la tangente).

Représentons l'extérieur de l'arc C sur l'extérieur du cercle $|z| > 1$ à condition de la correspondance des points infiniment éloignés. Dans cette transformation l'arc C' passera en une courbe fermée C_1 infiniment voisine du cercle $|z| = 1$. Il est évident que l'inégalité (2) se réduira à l'inégalité

$$f'(\infty, C_1) < 1.$$

Désignons par S_1 l'aire de la surface limitée par le cercle $|z| = 1$ et, à l'extérieur, par la courbe C_1, de même que par S_2 l'aire de la surface limitée par la courbe C_1 et le cercle $|z| = 1$, à l'extérieur. Alors on peut écrire, aux infiniment petits d'ordre supérieur par rapport aux aires S_1 et S_2 près (1), que

$$f'(\infty, C_1) = 1 - \frac{1}{2\pi}(S_1 - S_2).$$

Il en résulte que pour démontrer le théorème II il suffit de démontrer que $S_1 - S_2 > 0$, cette différence devant être un infiniment petit du même ordre que les aires S_1 et S_2.

Cette affirmation se déduit directement du lemme suivant, que nous donnons plus bas sans démonstration.

Lemme. *Soit donné un arc C dans un plan z. Désignons par $f'_+(z_0, C)$ et $f'_-(z_0, C)$ les limites de la dérivée $f'(z, C)$, lorsque le point z tend vers un point du contour z_0, respectivement du côté convexe et du côté concave de la courbe C. On a alors*

$$|f'_+(z_0, C)| > |f'_-(z_0, C)|.$$

Théorème III. *Soit donné un triangle ABD (les points A, B et D se suivent dans le sens direct de parcours). Soit de plus $\sphericalangle ABD < \frac{2}{3}\pi$. Alors de tous les arcs convexes s'appuyant sur la corde AD et situés sur le contour $\sphericalangle ABD$ ou bien à son intérieur, la fonctionnelle $\varphi[C; A]$ a un maximum pour la ligne brisée ABD.*

Nous donnons ci-dessous, sans le prouver, deux lemmes, dont il résulte directement la démonstration du théorème III.

Lemme 1. *Choisissons sur le côté AB un point arbitraire B' et construisons une ligne brisée $AB'D$. Désignons les lignes brisées ABD et $AB'D$ respectivement par C' et C''. Alors nous avons*

$$\varphi[C'; A] > \varphi[C''; A] \tag{3}$$

l'angle ABD étant inférieur à $\frac{2}{3}\pi$.

Lemme 2. *Soient K et K' deux courbes, ayant les extrémités A et B communes et, au moins, un point commun D. Supposons de plus que dans l'intervalle AD la courbe K' est au-dessus de K, et dans l'intervalle DB au-dessous de K. Alors, si l'on a*

$$\arg f(B, K) - \arg f(A, K) = \arg f(B, K') - \arg f(A; K')$$

l'inégalité

$$\varphi[K'; A] > \varphi[K; A] \tag{4}$$

est vérifiée.

Considérons maintenant une courbe arbitraire C satisfaisant aux conditions du théorème III. Choisissons un point B' tel que l'égalité

$$\arg f(D, C'') - \arg f(A', C'') = \arg f(D, C) - \arg f(A, C)$$

ait lieu.

On peut montrer d'après le principe de Montel que la ligne brisée C'' rencontre la courbe C. Comme la courbe C est convexe, les lignes C et C'' ne se rencontront qu'en un seul point, ce qui vérifie le lemme 2. Il suit des inégalités (3) et (4) que

$$\varphi[C'; A] > \varphi[C''; A] > \varphi[C; A], \quad \text{c. q. f. d.}$$

Les théorèmes II et III permettent de prouver le théorème suivant:

Théorème IV. *La ligne brisée ABD possède, parmi toutes les courbes convexes satisfaisantes aux conditions du théorème IV, la poussée maximum.*

Il en résulte que pour démontrer l'inégalité fondamentale (1) il suffit de la prouver pour la ligne brisée ANB tangente à la courbe $C: \overset{\frown}{AB}$ en points A et B. On peut montrer que l'inégalité (1) est juste pour une ligne brisée, en se servant de l'intégrale de Schwartz-Christofel. Notons que la marche de la démonstration exige l'emploi de l'inégalité

$$\frac{BN}{AN} > A(m)\alpha \tag{5}$$

qui résulte de la condition $k < \frac{m}{l}$, où $\alpha = \sphericalangle ANB$ et où $A(m)$ désigne une constante ne dépendant que de m et qui tend vers zéro lorsque m croît.

Il est donc évident que si l'on n'exige pas que la courbure soit limitée, la classe des courbes, pouvant être admises, comprendra les lignes brisées ne vérifiant pas l'inégalité (5). On peut encore montrer que pour ces lignes brisées l'inégalité (1) n'est pas toujours vérifiée.

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PHYSIK

ÜBER EINE NEUE ART DES TEILUNGSPROZESSES DES URANKERNES

Von V. G. CHLOPIN, Mitglied der Akademie, M. A. PASWIK-CHLOPIN und N. F. VOLKOV

Vor kurzem hat einer von uns([1]) gezeigt dass die Teilungsprodukte des Urans noch während 25 Stunden nach der Unterbrechung der Bestrahlung des Urans mit Neutronen nach der Methode des radioaktiven Rückstosses auf einer Glassplatte gesammelt werden können. Die einfachste Erklärung dieser Erscheinung besteht in der Annahme, dass ein mehr oder weniger langlebiges gasförmiges Teilungsprodukt irgendwo in der Mitte einer Umwandlungsreihe entsteht. Zugunsten einer solchen Annahme spricht auch die Tatsache, dass nach der Beendigung der Bestrahlung des Urans durch Neutrone, die nachfolgende Teilungsprodukte mit Hilfe der Rückstossmethode nicht nur von dem bestrahlten Uran sondern auch von seinen, während der Bestrahlung gesammelten Teilungsprodukten gewonnen werden konnten.

Um die obenerwähnte Annahme zu prüfen und die chemische Natur des postulierten gasförmigen Folgeproduktes zu bestimmen, haben wir folgende Experimente vorgenommen.

Circa 20 g Natriumpyrouranat, die sich in einer Glassröhre zwischen zwei Wattenpropfen befanden, wurden durch langsame Neutrone von einer konstanten aus circa 400 milligrammäquivalent Radiothorium+Berillium bestehenden Neutronenquelle während 17 Tagen bestrahlt. Neunzig Minuten nach der Beendigung der Bestrahlung wurde die Glassröhre mit dem Pyrouranat mit einer Wasserstrahlpumpe verbunden und durch das Präparat ein konstanter Strom reiner, d. h. radonfreier Luft, die vorläufig durch ein U-förmiges mit Silikagel gefülltes und bis $T° = -80°$ abgekühltes Glassrohr gezwungen wurde, während 25 Min. durchgesaugt. Dadurch sollte der Pyrouranat von dem etwaigen okkludierten Radon und den primären gasförmigen Teilungsprodukten des Urankernes befreit werden. Nachdem 25 Min. verflossen waren, wurde die Temperatur des Kriostaten auf $T° = -110°$ gebracht und zwischen dem Glassrohr mit dem Pyrouranat und der Wasserstrahlpumpe noch ein U-förmiges Glassrohr mit auf $T° = -110°$ abgekühltem Silikagel eingeschaltet. Das Durchsaugen der radonfreien Luft wurde alsdann noch während 4 Stunden fortgesetzt. Das zweite Glassrohr mit Silikagel diente zum Auffangen der gasförmigen Teilungsprodukte, falls solche sich während des Zerfalls der primärgebildeten Teilungsprodukte des Urans ansammeln können.

Nachdem der Luftstrom unterbrochen wurde, unterwarf man das Silikagel aus der zweiten U-förmigen Glassröhre einer chemischen Analyse.

Zu diesem Zwecke wurde das Silikagel mit verdünnter (1 : 5) Salzsäure ausgekocht, die Lösung, welche die etwaige (feste) Teilungsprodukte des Urans enthalten sollte, von dem Silikagel abfiltriert und in 50 cm^3 Wasser, das 0.2 g $BaCl_2 \cdot 2\,H_2O$, 0.3 g $SrCl_2 \cdot 6H_2O$ und 0.05 g $La(NO_3)_3$ aufgelöst enthielt, aufgefangen. Das Silikagel wurde mit heissem Wasser ausgewaschen, alsdann bei $T^c = 80—90^c$ getrocknet und für die nachfolgende Versuche verwendet.

Aus der Lösung wurde zuerst Lantan sammt anderen seltenen Erden mittels kohlensäurefreien Ammoniak als $La(OH)_3$ abgetrennt, mit heissem Wasser ausgewaschen, getrocknet und zur Messung gebracht. Das Filtrat von der Lantanfällung wurde mit Salzsäure schwach angesäuert, alsdann Kaliumchromat in kleinem Überschuss zugesetzt, und Natriumacetat solange zugegeben, bis das ganze Barium als Bariumchromat niedergeschlagen wurde.

Der Niederschlag wurde abfiltriert, mit Wasser ausgewaschen, in Salzsäure 1 : 5 auf dem Filter gelöst und aus der Lösung als Chromat nochmals umgefällt. Das ausgewaschene und getrocknete Bariumchromat wurde zur Aktivitätsbestimmung verwendet. Zum Filtrat nach der Bariumfällung wurde noch 0.1 g $BaCl_2 \cdot 2H_2O$ zugesetzt, wie oben beschrieben als Chromat gefällt, abfiltriert und aus dem Filtrat das Strontium als Sulfat nach der Zugabe von verdünnter Schwefelsäure und Alkohol abgeschieden. Das Strontiumsulfat wurde mit kaltem Wasser ausgewaschen, getrocknet und zur Messung gebracht. Die Aktivitätsmessungen geschahen mittels eines Geiger-Müller'schen Zählers aus Duraluminium mit einer Wandstärke von 0.12 mm.

Alle Niederschläge wiesen merkliche Aktivität auf. Die aufgenommenen Aktivitätszerfallkurven liessen vorläufig folgende radioaktive Isotope bestimmen.

In dem Lantan+Yttrium Niederschlage drei verschhiedene Radioelemente mit den Halbwertszeiten $T \sim 30^m$, $T \sim 9^h 30^m$ und $T \sim 45^h$. In Strontiumsulfat auch drei, mit $T \sim 20^m$, $T \sim 7^h 30^m$ und einer viel längeren Halbwertszeit und in Bariumchromat zwei Isotope mit $T \sim 10^h$ und $T \sim 50^h$. Die Aktivitätszerfallkurven wie bei Barium, so auch bei Strontium wiesen gleich nach der Abtrennung einen Aktivitätsanstieg auf, was auf die Bildung von Radiolantan im ersten Falle und Radioyttrium im zweiten deutet.

Das Auftreten von Radiobarium und Radiostrontium unter den Umwandlungsprodukten der in Silikagel aufgefangenen gasförmigen Teilungsprodukte des Urans weist eindeutig darauf hin, dass wir es nicht mit einem, sondern mit zwei gasförmigen Teilungsprodukten zu tun haben und zwar mit Xenon und Krypton.

Diese zwei neue radioaktive Isotope des Xenons und des Kryptons sind mit den früher von O. Hahn u. F. Strassmann[2] und A. Aten jun., C. Bakker und F. Heyn[3] aufgefundenen nicht identisch, da sie nicht als primäre Teilungsprodukte auftreten, sondern als sekundäre Umwandlungsprodukte sich in der Mitte einer Umwandlungsreihe bilden.

Damit kann als erwiesen gelten, dass ausser der früher bekannten Teilungstypen des Uranskernes unter der Einwirkung der Neutronen noch zwei neue Teilungstype existieren, bei denen Radioxenon und Radiokrypton als intermediäre Umwandlungsprodukte der primären Bruchstücke des Urankernes auftreten.

Als primäre Bruchstücke des Urankernes bei diesen zwei neuen Teilungstypen müssen Elemente auftreten, welche in dem Periodischen System links von Xenon und Krypton stehen. Das können entweder Brom und Jod, oder Selen und Tellur, oder Arsenik und Antimon, oder, schliesslich, Germanium und Zinn sein. Alle diese Elemente müssen wir unter Teilungsprodukten des Urankernes erwarten, da sie das eine primäre

Bruchstück des Urankernes bilden können; was das zweite primäre Bruchstück anbetrifft, so wird es entweder durch Lantan und Yttrium, oder Cerium und Zirkonium, oder Praseodymium und Niobium, oder Neodymium und Molybdenum vertreten.

Gleichzeitig kann als bewiesen gelten, dass die Teilungsprodukte des Urans Umwandlungsreihen bilden können, welche mindestens fünf aufeinanderfolgende β-Strahler enthalten (von Brom bis Yttrium, oder von Jod bis Lantan).

Die Bestimmung der Länge der β-Umwandlungsreihen ist insofern von Bedeutung, dass von deren Länge die Menge der bei der Urankernteilung freiwerdenden Neutronen abhängt. Zur Zeit werden Versuche vorgenommen, die zum Zweck haben, die bei den zwei neu aufgefundenen Teilungstypen des Urans auftretende primäre Bruchstücke des Urankernes aufzufinden und die Halbwertszeiten der beiden neuen radioaktiven Isotopen des Xenons und des Kryptons näher zu bestimmen.

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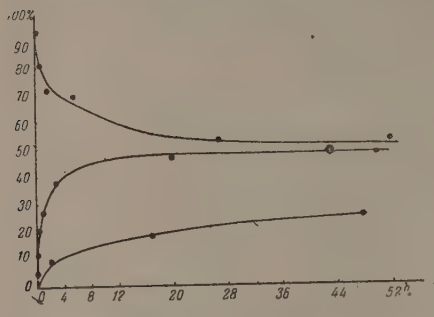
PHYSICS

EXCHANGE OF THE BROMINE IONS BETWEEN AgBr AND THE BROMIDE SOLUTION

By A. POLESSITSKY

(Communicated by V. G. Chlopin, Member of the Academy, 22. VII. 1939)

In a previous paper (1) I have shown that a full exchange of the bromine ions between the freshly coagulated AgBr and KBr solution takes place within several minutes. As Breshneva and Roginsky(2) failed to observe any exchange at room temperature, I repeated the exchange experiments at 20°C. For this purpose 1 g of AgBr, obtained through mixing of equivalent amounts of $AgNO_3$ and KBr, was coagulated by stirring, filtered off and treated with 10 cm³ of the solution of an equivalent amount of KBr. One of the components (AgBr or KBr) contained radioactive bromine Br*. AgBr was filtered off after different intervals and measured with the help of a Geiger-Müller counter. KBr precipitated from the filtrate as AgBr and was subjected to measurement, too.



The distribution of the radioactive bromine between the components points to the degree of exchange. The results of the experiment are shown in the figure. Curve *a* shows the decrease in AgBr* radioactivity during the exchange with inactive KBr. Curve *b* shows the increase in the content of radioactive bromine in the inactive AgBr through the exchange with radioactive KBr*. Both curves reach the same limit corresponding to equal amounts of the radioactive atoms present in both components.

At the beginning the exchange proceeds very rapidly. Within one minute 10% of the radioactive atoms pass to the other component. However, further on the rate of the exchange drops abruptly, and a full exchange requires 20—30 hours to be achieved. The decrease of the exchange rate is evidently due to the «ageing» of the precipitate.

Other experiments done with precipitates that were left to «age» during 2 days showed much lower rates of exchange (curve *c*). Melted AgBr showed no exchange of bromine with KBr solution during 2 days.

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PHYSIQUE

DU NOMBRE DE CYCLES LIMITES NAISSANT EN CAS DE VARIATION DES COEFFICIENTS D'UN ÉTAT D'ÉQUILIBRE DU TYPE FOYER OU CENTRE

Par N. BAUTIN

(Présenté par L. I. Mandelstam, de l'Académie, le 1. VII. 1939)

Cette Note pose la question: quel est le nombre maximum de cycles limites que peut engendrer un état d'équilibre de type foyer ou centre du système

$$\frac{dx}{dt} = \sum_{i+k=1}^{i+k=n} a_{ik} x^i y^k, \qquad \frac{dy}{dt} = \sum_{i+k=1}^{i+k=n} b_{ik} x^i y^k \; (a_{10}b_{01} - a_{01}b_{10} \neq 0) \qquad (A_n)$$

$n\,(n \geqslant 1)$ étant un nombre entier fixé, en cas de variation quelconque des coefficients a_{ik}, b_{ik}, et la résout pour $n=2$. Pour $n=2$ ce nombre maximum de cycles est de 3. Par là même est indiqué un exemple de système (A_2) ayant 3 cycles limites *.

§ 1. Choisissons un nombre n déterminé. Tout ensemble de valeurs des coefficients du système (A_n)

$$a_{ik},\ b_{ik}\,(i, k = 0, 1, 2 \ldots n;\ 1 \leqslant i+k \leqslant n)$$

peut être considéré comme un point d'un espace euclidien $E_n = E^{n(n+3)}$. A chaque système de la forme (A_n) correspond un point de l'espace E_n et réciproquement.

Définition. Nous dirons que l'état d'équilibre $x=0$, $y=0$ du système (A_n) de coefficients donnés satisfaisant les conditions $a_{10}b_{01} - a_{01}b_{10} > 0$ et $a_{10}+b_{01}=0$ ** est par rapport à l'espace E_n cyclique d'ordre $k\,(k \geqslant 0)$, si:

a) On peut indiquer $\varepsilon_0 > 0$, $\delta_0 > 0$ tels que dans le voisinage ε_0 du point de l'espace E_n correspondant au système (A_n) donné il n'existe pas de point correspondant à un système de la forme (A_n) ayant à l'intérieur du voisinage δ_0 du point $x=0$, $y=0$ du plan x, y plus de k cycles limites.

b) Quels que soient les nombres positifs $\varepsilon < \varepsilon_0$, $\delta < \delta_0$, on peut toujours indiquer à l'intérieur du voisinage ε du point de l'espace E_n qui

* A ce que je sais, il n'avait pas encore été indiqué d'exemples de systèmes (A_2) ayant plus de 1 cycle limite. Le premier exemple d'équations ayant pour $n=2$ un cycle limite a été donné par Frommer [1].

** Une partie des coefficients a_{ik}, b_{ik} $(1 < i+k \leqslant n)$, ou même tous ces coefficients, peuvent être nuls.

correspond au système (A_n) donné un point auquel correspond un système de la forme (A_n) ayant à l'intérieur du voisinage δ du point $x=0$, $y=0$ k cycles limites.

§ 2. Si $a_{10}b_{01}-a_{01}b_{10}>0$ et $(a_{10}-b_{01})^2+4a_{10}b_{01}<0$, le système (A_2) peut toujours être ramené à la forme

$$\left.\begin{aligned}\dot{x}&=\lambda_1 x-y-\lambda_3x^2+(2\lambda_2-\lambda_5)\,xy+\lambda_6y^2,\\ \dot{y}&=x+\lambda_1y+\lambda_2x^2+(2\lambda_3+\lambda_4)\,xy-\lambda_2y^2.\end{aligned}\right\}\qquad (B)$$

Posant $x=\rho\cos\varphi$, $y=\rho\sin\varphi$, passons aux coordonnées polaires et cherchons la solution sous forme de série ordonnée suivant les puissances de la valeur initiale ρ_0. Le segment de la droite $\varphi=0$ sera pour toutes les valeurs suffisamment petits de ρ un segment sans contact. Posant $\varphi=2\pi$, nous trouverons sur un segment suffisamment petit $\varphi=0$, $0\leqslant\rho_0\leqslant r$, la fonction de conséquence

$$\rho=\rho_0u_1(2\pi)+\rho_0^2u_2(2\pi)+\rho_0^3u_3(2\pi)+\ldots \qquad (1)$$

Lemme 1. Les coefficients $u_i(2\pi)$ sont des fonctions entières des paramètres λ_ν.

Lemme 2. La condition $u_1(2\pi)=1$, $u_3(2\pi)=u_5(2\pi)=u_7(2\pi)=0$ suffit pour que l'on ait $u_i(2\pi)=0$ $(i=2,3,4,\ldots)$.

En effet, toute solution du système $u_1(2\pi)=1$, $u_3(2\pi)=u_5(2\pi)=u_7(2\pi)=0$ se confond avec les conditions de centre pour le système (B) établies par Dulac [2] et Kapteyn [3] *.

Lemme 3. Les coefficients $u_i(2\pi)$ sont de la forme:

$$u_1(2\pi)=e^{2\pi\lambda_1};\quad u_2(2\pi)=\lambda_1\theta_2^{(1)};\quad u_3(2\pi)=\bar{u}_3+\lambda_1\theta_3^{(1)};$$
$$u_4(2\pi)=\bar{u}_3\theta_4^{(3)}+\lambda_1\theta_4^{(1)};$$
$$u_5(2\pi)=\bar{u}_5+\bar{u}_3\theta_5^{(3)}+\lambda_1\theta_5^{(1)};\quad u_6(2\pi)=\bar{u}_5\theta_6^{(5)}+\bar{u}_3\theta_6^{(3)}+\lambda_1\theta_6^{(1)};$$
$$u_7(2\pi)=\bar{u}_7+\bar{u}_5\theta_7^{(5)}+\bar{u}_3\theta_7^{(3)}+\lambda_1\theta_7^{(1)};$$
$$u_i(2\pi)=\bar{u}_7\theta_i^{(7)}+\bar{u}_5\theta_i^{(5)}+\bar{u}_3\theta_i^{(3)}+\lambda_1\theta_i^{(1)}\qquad (i>7)$$

où

$$\bar{u}_3=\frac{\pi}{4}\lambda_5(\lambda_3-\lambda_6),\qquad \bar{u}_5=\frac{\pi}{24}\lambda_2\lambda_4(\lambda_3-\lambda_6)(\lambda_4+5\lambda_3-5\lambda_6),$$
$$\bar{u}_7=\frac{25\pi}{32}\lambda_2\lambda_4(\lambda_3-\lambda_6)^2(\lambda_3\lambda_6-2\lambda_6^2-\lambda_2^2),$$

les θ étant des fonctions entières de λ_ν.

Les propositions relatives aux coefficients u_i $(i>7)$ se démontrent comme suit.

En vertu des lemmes 1 et 2 et des conditions de centre on a

$$u_i(2\pi)=\lambda_2\lambda_4(\lambda_3-\lambda_6)(\lambda_3\lambda_6-2\lambda_6^2-\lambda_2^2)\,\theta_i+\bar{u}_5\theta_i^{(5)}+\bar{u}_3\theta_i^{(3)}+\lambda_1\theta_i^{(1)}\quad (i>7)$$

où les θ_i peuvent être considérés comme indépendants de λ_4. Pour trouver la forme définitive de u_i nous montrerons que le développement de θ_i, suivant les puissances de $\mu=\lambda_3-\lambda_6$, commence par un terme de degré au moins égal à 1. Il suffit de prendre le cas où $\lambda_1=\lambda_5=\lambda_4+5\mu=0$ et de montrer que le développement de μ commence par des termes de degré moins ou égal à 3.

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* Le travail beaucoup plus récent de Frommer [1], dans sa partie concernant les conditions de centre, ne peut être pris en considération, car le cas

$$\lambda_1=\lambda_5=\lambda_4+5\lambda_3-5\lambda_6=\lambda_3\lambda_6-2\lambda_6^2-\lambda_2^2=0$$

y est classé comme foyer, alors que c'est un cas de centre.

Le système (B) prend dans ce cas la forme

$$\left.\begin{aligned} \dot{x} &= -H'_y + \mu p = -(y - \lambda_6 x^2 + 2\lambda_2 xy + \lambda_6 y^2) - \mu x^2 \\ \dot{y} &= H'_x - \mu q = x + \lambda_2 x^2 + 2\lambda_6 xy - \lambda_2 y^2 - 3\mu xy. \end{aligned}\right\} \quad (C)$$

Considérons une courbe fermée C_{h_0} de la famille $H(x, y) = h$, coupant le segment $\varphi = 0$ en un point $\rho_0 < r$, et introduisons dans le voisinage de C_{h_0} les coordonnées δ et s:

$$H(x, y) = h_0 + \delta, \quad n(x, y; s) = 0$$

où, quel que soit s, $n(x, y; s) = 0$ est un arc sans contact qui se confond lorsque $s = 0$ avec le segment $\varphi = 0$, et s — une coordonnée cyclique telle que $\frac{ds}{dt} = 1$ sur la courbe C_{h_0}.

Nous cherchons la solution de l'équation transformée (C) sous forme de série ordonnée suivant les puissances de μ et de la valeur initiale δ_0. Posant en suite $s = \tau$, où τ est la période sur la courbe C_{h_0}, nous obtenons sur un segment $s = 0$ la fonction de conséquence

$$\delta = \delta_0 + \mu^2 [\alpha_{02}(\tau) + \alpha_{12}(\tau)\delta_0 + \alpha_{03}(\tau)\mu + \ldots].$$

Demander que le développement de $\rho - \rho_0$ suivant les puissances de μ ne contienne pas, à la condition $\lambda_1 = \lambda_5 = \lambda_4 + 5\mu = 0$, de termes de degré inférieur à 3 équivaut à demander que le coefficient

$$\alpha_{02} = \int_0^\tau \left[(p'_x + q'_y) \int_0^s (\dot{y}p - \dot{x}q)\, dt \right] ds \quad (2)$$

soit nul quelle que soit la courbe C_{h_0}.

Prenant en considération que le système $\dot{x} = -H'_y + \mu p$, $\dot{y} = H_x + \mu q$ reste conservatif si

$$p = xy, \ q = 0; \quad p = 0, \ q = xy; \quad p = -x^2, \ q = 2xy$$

et que, par conséquent, dans ces conditions tous les $\alpha_{ij} = 0$, on trouve d'après les conditions $\alpha_{01} = \alpha_{11} = \alpha_{02} = 0$

$$\int_0^\tau x\dot{x}ds = 0; \quad \int_0^\tau y\dot{y}ds = 0; \quad \int_0^\tau xy\dot{y}ds = 0; \quad \int_0^\tau x^2\dot{y}ds = 0;$$

$$\int_0^\tau \left[x \int_0^s xy\dot{x}dt \right] ds = 0. \quad (3)$$

De plus (égalités évidentes)

$$\int_0^\tau \dot{x}ds = 0, \quad \int_0^\tau x\dot{x}ds = 0, \quad \int_0^\tau x^2\dot{x}ds = 0, \quad \int_0^\tau y\dot{y}ds = 0,$$

$$\int_0^\tau (x\dot{y} + \dot{x}y)\, ds = 0. \quad (4)$$

Dans (2), (3) et (4) $x = \varphi(t)$, $y = \psi(t)$ sont les équations de la même courbe C_{h_0}. (2), (3) et (4) ont lieu quelle que soit la courbe C_{h_0}. Remarquant que $x = \varphi(t)$, $y = \psi(t)$ satisfont le système (C) lorsque $\mu = 0$ et utilisant (2), (3) et (4), nous trouvons $\alpha_{02} = 0$.

§ 3. D'après le lemme 3

$$\rho - \rho_0 = \rho_0 (2\pi\lambda_1\psi_1 + \bar{u}_3\psi_3\rho_0^2 + \bar{u}_5\psi_5\rho_0^4 + \bar{u}_7\psi_7\rho_0^6)$$

les ψ_i étant des séries ordonnées suivant les puissances de ρ_0 et telles que $\psi_i(0) \neq 0$. Il est facile maintenant de montrer que quel que soit le point λ_ν de l'espace des coefficients du système (B), on peut toujours indiquer $\varepsilon_0 > 0$ et $\delta_0 > 0$ tels que, pour tous les points du voisinage ε_0 du point considéré de l'espace des coefficients, $\rho - \rho_0$ ne possède pas plus de 3 racines, positives à l'intérieur du voisinage δ_0 de l'origine. D'autre part: quels que soient $\varepsilon < \varepsilon_0$ et $\delta < \delta_0$, il existe toujours dans le voisinage ε du point de l'espace des coefficients, où $\lambda_1 = \lambda_5 = \lambda_4 + 5\lambda_3 - 5\lambda_6 = 0$, des points auxquels correspondent les systèmes de la forme (B) ayant dans le voisinage δ de l'origine 3 cycles limites. Si au point considéré de l'espace des coefficients $\lambda_1 = \bar{u}_3(2\pi) = 0$, $\bar{u}_5(2\pi) \neq 0$ ou $\lambda_1 = 0$, $\bar{u}_3(2\pi) \neq 0$, on a respectivement $k = 2$ ou $k = 1$.

Théorème. *Le système* (A_2) *peut posséder des états d'équilibre du type foyer ou centre cycliques par rapport à l'espace* E_2 *d'ordre* 1, 2 *ou* 3 *et ne possède pas d'états d'équilibre cycliques par rapport à l'espace* E_2 *d'ordre supérieur à* 3.

Je tiens à exprimer ma gratitude à E. Léontovitch qui a bien voulu m'aider dans ce travail, ainsi qu'au Prof. A. Andronov, à qui je dois la position du problème.

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PHYSIQUE

DE TRAJECTOIRES SUR LES SURFACES ORIENTÉES

Par A. MAYER

(Présenté par L. I. Mandelstam, de l'Académie, le 1. VII. 1939)

§ 1. Soit donné dans l'espace euclidien à trois dimensions R_3 une surface analytique S_n du genre n orientée et fermée. Soit S_n couverte d'un nombre fini de domaines g, dans chacun desquels est défini un système de coordonnées (φ, ψ). On suppose:

1) en déduisant la métrique S_n de la métrique R_3 que les coefficients E, F, G de la forme quadratique fondamentale satisfont à la condition

$$EF - G^2 < 0$$

(la distance entre deux points de S_n sera prise comme distance géodésique sur S_n);

2) que le passage d'un système de coordonnées (φ, ψ) à un autre système dans les points communs des différents domaines g se fait à l'aide des fonctions continues, ayant des dérivées continues et la jacobienne non nulle.

Soit donné sur S_n un système d'équations différentielles défini de la manière suivante:

a) dans tout domaine séparé, le système a la forme

$$\frac{d\varphi}{dt} = \Phi(\varphi, \psi), \quad \frac{d\psi}{dt} = \Psi(\varphi, \psi)$$

où les parties de droite satisfont aux conditions de la théorie de Cauchy et ne sont nulles simultanément qu'à un nombre fini de points;

b) dans les points, communs à deux ou plusieurs domaines g, le passage des unes équations aux autres se fait à l'aide d'une transformation, effectuant le passage d'un système de coordonnées à l'autre.

Dans ces conditions nous pouvons parler dans le sens ordinaire des trajectoires, demi-trajectoires, d'états d'équilibre etc. sur S_n et on peut tracer en tout point de S_n, n'étant pas un état d'équilibre de trajectoires, un arc sans contact. D'après la condition a) il ne peut être sur S_n qu'un nombre fini d'états d'équilibre; nous supposerons de plus qu'il n'existe qu'un nombre fini de cycles limites et de séparatrices. Nous comprendrons sous le cycle limite des trajectoires fermées dont le voisinage aussi proche que l'on veut contient non seulement des points appartenant aux trajectoires fermées. On appelera séparatrices des trajectoires pouvant être prolongées, au moins d'un côté, au délà d'un état d'équilibre dans le sens de Bendixson[1].

Dans ces suppositions sont données les propriétés des trajectoires fermées stables sur S_n dans le sens de Poisson (§2). On y examine la position récipro-

que des formations limites et d'autres trajectoires, de même qu'on résout dans un certain sens la question de la structure qualitative de divisions de la surface en trajectoires (§4)*.

§ 2. Théorème I. *Soit $L_+(L_-)$ une demi-trajectoire positive (négative) sur S_n, ayant un point limite M, distinct d'un état d'équilibre et étant limite pour quelqu'une des demi-trajectoires. Alors $L_+(L_-)$ est stable dans le sens de Poisson.*

Théorème II. *Si une demi-trajectoire L_+ non-fermée, stable d'après Poisson sur S_n, a parmi ses ω points limites une demi-trajectoire $L'_+(L'_-)$ non-fermée, $L'_+(L'_-)$ a parmi ses $\omega(\alpha)$ points limites une demi-trajectoire L_+.*

Théorème III. *Il ne peut exister sur S_n plus de n demi-trajectoires non-fermées, stables d'après Poisson, et telles qu'aucune d'elles n'est limite pour quelqu'une autre.*

On démontre ces trois théorèmes par le passage aux surfaces ayant des frontières composées d'arcs sans contact et d'arcs de trajectoires. On se sert dans ce cas de la méthode de l'entière induction—le genre de la trajectoire s'abaisse moyennant la coupure de la surface, le nombre de frontière étant accru**.

§ 3. Pour étudier ce que deviennent les trajectoires n'étant pas limites pour d'autres trajectoires, rappelons nous la définition de la stabilité orbitale(6).

Une demi-trajectoire $L_+(L_-)$ est stable $\omega(\alpha)$ orbitalement en un point M, si l'on peut choisir pour $\varepsilon > 0$ quelconque un $\delta > 0$ tel que toutes les demi-trajectoires positives (négatives), traversant le voisinage δ de M, ne sortent pas, si l'on les prolonge, du voisinage ε de la partie $L_+(L_-)$ succédant (précédent) à M.

On démontre que si $L_+(L_-)$ est stable $\omega(\alpha)$ orbitalement en un quelconque de ses points, elle le sera de même en tout autre de ses points.

Théorème IV. *Soient L une trajectoire fermée et CA un arc sans contact, passant par son point C. Alors on a*: 1) *ou bien toutes les trajectoires coupant une partie suffisamment petite de CA'' de l'arc CA sont fermées*; 2) *ou bien par tous les points de la partie suffisamment petite CA'' de l'arc CA passent les demi-trajectoires, n'ayant pour points limites $\omega(\alpha)$ que les points de L. Elles seront toutes stables $\omega(\alpha)$ orbitalement.*

Théorème V. *Si une demi-trajectoire L_+ a parmi ses ω points limites une courbe fermée, formée de séparatrices et d'états d'équilibre, elle n'a pas d'autres points ω limites et est ω orbitalement stable.*

Théorème VI. *Si une demi-trajectoire L_+ non-fermée n'est ni séparatrice ni un état d'équilibre et si elle n'a pas parmi ses ω points limites de points appartenant aux demi-trajectoires non-fermées, stables d'après Poisson, elle est stable ω orbitalement et tend*: a) *ou bien vers un état d'équilibre sans pouvoir être prolongée au délà de cet état d'équilibre*; b) *ou bien vers une trajectoire fermée*; c) *ou bien vers une courbe fermée composée de séparatrices et d'états d'équilibre.*

Le premier des théorèmes IV, V et VI justifie le terme «cycle limite» introduit dans le § 1; le dernier est la suite des théorèmes I, IV et V.

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* On sait que H. Poincaré(2) a établi, en cas de tore, l'éxistence de trajectoires non-fermées, stables d'après Poisson. Il a montré leur rôle comme trajectoires limites en cas d'absence d'états d'équilibre, ce qui a été étudié d'une façon plus approfondie par Kneser(3) et Denjoy(4). Ce dernier en particulier a établi la dépendance entre le côté qualitatif des trajectoires et la nature analytique des membres de droite du système. Le théorème correspondant de Denjoy ne s'étend pas sur le cas de présence d'états d'équilibre, comme il suit de l'exemple de Cherry(5).

** L'énoncé du théorème I doit être completé de la condition que le point M n'appartienne pas à la frontière.

Théorème VII. *Si une demi-trajectoire L_+ non-fermée, stable d'après Poisson, rencontre un arc quelconque sans contact dans un ensemble de points, pas dense sur cet arc et non-vide, alors:*

1°. *Elle coupe tout autre arc sans contact dans un ensemble de points nullepart dense sur cet arc ou bien vide.*

2°. *Ils existent des demi-trajectoires, ayant L_+ parmi ses $\omega(\alpha)$ points limites et n'étant pas stables d'après Poisson.*

3°. *Ces demi-trajectoires sont $\omega(\alpha)$ orbitalement stables et n'ont pas d'autres points limites, sauf ceux de L_+ et de ses limites*.*

Théorème VIII. *Si une demi-trajectoire L_+, stable d'après Poisson, rencontre un arc quelconque sans contact dans un ensemble de points dense partout sur cet arc, l'on a:*

1°. *Elle est dense partout dans un certain domaine G^* et est de plus ω orbitalement stable.*

2°. *Toute demi-trajectoire ayant L_+ parmi ces $\omega(\alpha)$ points limites est dense partout dans G^*, est $\omega(\alpha)$ orbitalement stable, et $\omega(\alpha)$ stable d'après Poisson.*

§ 4. Théorème IX. *La surface S_n, dans les conditions indiquées en § 1, se divise en domaines des types suivants:*

1. *Domaines, contenant des trajectoires non-fermées, orbitalement stables. Ces régions sont planes** et pas plus que biconnexes. Toutes les trajectoires d'une même région possèdent les mêmes $\omega(\alpha)$ points limites***.*

2. *Domaines, contenant des trajectoires fermées. Une telle région sera du type plane et pas plus que deux fois biconnexe; ou bien, pour $n=1$ (un tore) peut occuper toute la surface.*

3. *Domaines, partout densement remplis de trajectoires non-fermées, stables d'après Poisson. Ces domaines ne sont pas planes et leur nombre est inférieur à n.*

Les autres trajectoires de S_n servent de frontières aux domaines indiqués.

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* Cette affirmation se démontre le plus facilement en se servant de l'inégalité déduite dans la condition 1° du § 1.

** Dans ce sens que chaque courbe fermée et simple la divise.

*** En cas de transformation d'une surface fermée en elle-même, Smith[7] a démontré un théorème analogue, se rapportant aux composantes régulières.

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PHYSICS

AN INVESTIGATION OF THE FREQUENCY OF THE O—H GROUP IN BINARY MIXTURES BY THE METHOD OF COMBINATION DISPERSION

By V. I. MALYSHEV

III. COMBINATION SPECTRA OF SOLUTIONS OF METHYL ALCOHOL IN BENZENE, CHLOROBENZENE, FLUOROBENZENE, ACETONE, DIOXENE, ETHYL ETHER, ISOAMYL ETHER, PYRIDINE AND PIPERIDINE

Solutions of methyl alcohol (CH_3OH) in CCl_4 and $CHCl_3$ were investigated in a previous work(1). It was shown that at low concentrations the alcohol molecules do not influence one another. Further, it was established that the electrical moment of molecules of $CHCl_3$ does not cause much disturbance in the oscillations of O—H. The only influence of the moment consisted in hindering the association of alcohol molecules.

In the subsequent investigations we attempted to elucidate the manner, in which the various molecular characteristics of the interacting molecules influence the disturbance of the oscillation of O—H. To this end we investigated solutions of CH_3OH in various solvents, the molecules of which have electrical moments of different magnitudes, different structures and which contain different atoms. The results of these investigations are given in the present work.

All the solutions mentioned below were of low concentration (2, 5, 10%), since it is only at such concentrations that the alcohol molecules do not interact with one another, so that it is easy to establish the influence of the molecules of the solvent on the oscillation of the O—H group of the alcohol molecules.

1. Solutions of CH_3OH in Benzene, C_6H_6. In distinction from the molecules of CCl_4 and $CHCl_3$ which have a tetrahedral structure, benzene has a plane structure in the form of a hexagonal ring. Benzene molecules have zero moment. We investigated the dispersion spectra of solutions of CH_3OH with concentrations of 3.5, 5 and 10%. On all the spectra of these solutions there is observed a slight widening of the frequency line $\nu = 3611\ cm^{-1}$ corresponding to oscillation of the O—H group of the CH_3OH molecule. The frequency of this line is close to that of the line observed with solutions in CCl_4 and $CHCl_3$. The band of associated molecules appears at greater concentrations (10%) than is the case with solutions in CCl_4. Hence it may be concluded that the benzene molecules hinder the association of the alcohol molecules to a greater extent than do the molecules of CCl_4.

2. Solutions of CH_3OH in Chlorobenzene, C_6H_5Cl. The chlorobenzene molecule has the same structure as the benzene molecule. The moment of the chlorobenzene molecule is $\mu = 1.5 \times 10^{-18}$. Concentrations

of 4, 10 and 20% were investigated. On the spectra we observed lines of frequency $\nu = 3630$ cm^{-1}, of approximately the same width as with solutions in benzene. The presence of a moment was displayed by the appearance of bands at still greater concentrations (20%) than was the case with solutions in benzene.

3. Solutions of CH_3OH in Fluorobenzene, C_6H_5F. Here the moment $\mu = 1.4 \times 10^{-18}$. The results are analogous with those obtained with solutions in chlorobenzene. Widening of the frequency line $\nu = 3633$ cm^{-1} is observed. Thus, the replacement of chlorine by fluorine in the benzene ring does not affect the disturbance of the oscillations of O—H in the alcohol molecule.

Attempts to investigate solutions of CH_3OH in bromobenzene, C_6H_5Br, were unsuccessful owing to the intense decomposition of bromobenzene by light. However, it may be supposed that the results would have been analogous with those obtained with chloro- and fluorobenzene.

4. Solutions of CH_3OH in Acetone, CH_3COCH_3. The acetone molecule has a great electrical moment $\mu = 2.7 \times 10^{-18}$, higher in magnitude than that of the alcohol molecules; furthermore, an atom of oxygen enters into the composition of the acetone molecule. The concentrations investigated were 4, 10 and 20%. A comparatively wide band with a maximum at $\nu = 3532$ cm^{-1} is observed in the spectra of these solutions. In position this band lies approximately half way between the maximum of the band of pure alcohol and the lines observed with low concentration solutions in CCl_4.

Thus, oscillation of the O—H group of the alcohol molecules is disturbed by the acetone molecules in a different manner compared to how all the above-mentioned molecules disturb it. The explanation of this must be sought either in the greater value of the electrical moment, or in the presence of an oxygen atom which disturbs the group O—H considerably, possibly, by the formation of a hydrogen bond. In order to elucidate this we investigated solutions of CH_3OH in substances, the molecules of which contain oxygen, but which have a small electrical moment.

5. Solutions of CH_3OH in Dioxane, $C_4H_8O_2$. The dioxane molecule has an hexagonal ring structure with oxygen in a para-position. The resultant moment of the dioxane molecules is zero. However, even if it is supposed that the alcohol molecules approach so closely to the dioxane molecules that the moment of the para-group cannot be considered as compensated, the magnitude of the effective moment will nevertheless be smaller than in the case of the acetone molecule. Concentrations of 2, 3, 5 and 10% were investigated. The results are analogous with those obtained with solutions in acetone. A band appeared with a maximum at $\nu = 3516$ cm^{-1}. However, in the case of 2 and 3.5% concentrations the band is double and is similar to the band observed with solutions of water in dioxane([2]). A specific influence of dioxane was evidently displayed in this case. In the case of a 10% concentration the spectrograms of CH_3OH in acetone, CH_3OH in dioxane and H_2O in dioxane are quite analogous. In a 10% solution there are still no bands of associated molecules of alcohol.

6. Solutions of CH_3OH in Ethyl Alcohol, $(C_2H_5)_2O$. Here the moment $\mu = 1.1 \times 10^{-18}$. The spectrograms display a band with a maximum at $\nu = 3516$ cm^{-1} analogous with the band in solutions in acetone.

Further we investigated solutions of CH_3OH in isoamyl ether, $(C_5H_{11})_2O$, in the molecules of which the oxygen is screened by the presence of a large number of carbon and hydrogen atoms. In spite of the background which develops, it is easy to observe a band situated in the same position as with solutions in ethyl alcohol. It thus follows from experiments 4, 5 and 6 that

the presence of oxygen in the molecule of the solvent causes a similar disturbance of the oscillations of the O—H groups of the alcohol molecules in spite of the difference in the electrical moment.

7. Solutions of CH_3OH in Pyridine, C_5H_5N. The pyridine molecule is a hexagonal ring structure. An atom of nitrogen enters into its composition. The moment is $\mu = 2.3 \times 10^{-18}$. Concentrations of 5 and 10% were investigated. A band with a maximum at $\nu = 3406$ cm^{-1} was observed on the spectrograms. The band observed is similar in positions and form to that observed with solutions of water in pyridine([2]).

Further we investigated solutions of CH_3OH in piperidine, $C_5H_{11}N$. Here the moment $\mu = 1.2 \times 10^{-18}$. The results observed are analogous with those observed with solutions in pyridine, but it was impossible to measure accurately the maximum of the band obtained, owing to the presence of piperidine lines in the investigated part of the spectrum.

Thus, a nitrogen atom in the solvent molecules also causes appreciable disturbance of the oscillations of O—H. If we take the displacement of the maximum of the O—H band from its position in the case of alcohol vapour as a measure of the degree of disturbance of the oscillations of O—H, it may be stated that an oxygen atom in the solvent causes intense disturbance, but that a nitrogen atom causes even more intense disturbance.

The results of the observations are given in a table. The positions of the maxima of the bands and the widths of the half intensities were carried out from photomicrograms obtained with a Zeiss photomicrometer.

Solution	$\mu \times 10^{-18}$ molecules of solvent	ε of solvent	Position of max. of bands in cm^{-1}	Width of bands in cm^{-1}	Displacement from CH_3OH vapour line	Note
CH_3OH vapour	1.67	—	3672	—	0	Fine line
CH_3OH liquid	—	33.0	3377	~348	295	Wide band
1% in CCl_4	0	2.2	3647	~ 18	25	Thin line
1% in $CHCl_3$	1.15	5.0	3630	~ 30	42	Line
10% in CCl_4	—	—	3647	~ 18	25	Line and band. Band
			3363	~350	309	more intense than line
10% in $CHCl_3$	—	—	3630	~ 30	42	Line more intense
			3417	~200	255	than band
10% in C_6H_6	0	2.3	3611	~ 64	61	Widened line
10% in C_6H_5Cl	1.5	11.0	3630	~ 50	42	» »
10% in C_6H_5F	1.4	—	3633	~ 72	39	» »
10% in CH_3COCH_3	2.7	21.4	3532	~190	140	Band
10% in $C_4H_8O_2$	0	2.2	3516	~220	155	»
5% in $(C_2H_5)_2O$	1.1	4.0	3516	~100	155	»
5% in C_5H_5N	2.3	—	3406	~200	266	»

From a comparison of the results given in the table it follows that all the solvents investigated may be divided into two classes according to their disturbing influence on the oscillations of the O—H groups of the alcohol molecules: i. e. solvents the molecules of which contain oxygen or nitrogen atoms, and solvents the molecules of which do not contain these atoms. The former give an intensely displaced wide band with a maximum at $\nu = 3520$ cm^{-1} in the case of oxygen and at $\nu = 3406$ cm^{-1} in the case of nitrogen. The latter give a less displaced line, more or less widened, at a frequency of $\nu = 3630$ cm^{-1}.

So intense a disturbing action of oxygen and nitrogen on the oscillations of O—H may be attributed to the formation of a hydrogen bond between the hydroxyl group of the alcohol molecule and the oxygen or nitrogen molecule of the solvent. The wide band characteristic of oscillations of hydroxyl observed with pure alcohols in water is attributed by us to the association of identical molecule by the formation of hydrogen bonds. The present investigation shows that analogous intense disturbances may also take place in the case of different molecules, provided that one of them has an O—H group and the other an atom of oxygen or nitrogen.

The folowing experiment was carried out in order to confirm this. A 2% solution of CH_3OH in CCl_4 was made; in its spectrum we observed sharp lines of isolated molecules of alcohol and very weak traces of a band. Then 5% of acetone was added to this solution. The alcohol line was much weakened in the spectrum of this triple mixture, and an intense band appeared, different in position from the band of pure alcohol. The maximum of the band had a frequency of $\nu = 3528\ cm^{-1}$, i. e. the same as with solutions of CH_3OH in acetone. This result may be explained in the following way: in a 2% solution of CH_3OH in CCl_4 the probability of association of the alcohol molecules is low and there therefore exist preferentially isolated molecules. If the alcohol molecules can associate with the acetone molecules, we would increase the probability of association by the addition of acetone and then there appears the wide band characteristic of associated molecules, in which the oscillation of O—H is intensely disturbed by the formation of a hydrogen bond.

In the triple mixture of 2% CH_3OH and 5% pyridine, C_5H_5N, in CCl_4 there is also observed a weakening of the alcohol line and the appearance of a band in the same position as with solutions of CH_3OH in pyridine.

In conclusion the author wishes to express his profound gratitude to Prof. G. S. Landsberg, under whose guidance the present work was carried out.

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PHYSICS

MAGNETOTHERMAL PROPERTIES OF SOME ANOMALOUS PARAMAGNETIC SALTS AT LOW TEMPERATURES

By G. A. MILJUTIN and S. S. SHALYT

(Communicated by S. I. Wawilow, Member of the Academy, 3. VII. 1939)

The anhydrous salts $FeCl_2$, $CoCl_2$ and $CrCl_3$ show anomalous magnetic properties at low temperatures(1). It was therefore of interest to investigate the magnetothermal properties of these salts, viz. the so-called magnetocaloric effect and the influence of the internal magnetic field on the position of the specific heat jump(2) in the temperature region of the magnetic anomalies.

The investigation was carried out with the aid of a vacuum calorimeter, already described at length in papers on the investigation of specific heat(2).

Fig. 1 represents the dependence of the reversible variation of the temperature on the square of the magnetization under adiabatic magnetization or demagnetization of the salt in the anomalous temperature region. As seen from this figure, the magnetocaloric effect in $FeCl_2$ and $CoCl_2$ is negative, i. e. the salt cools under adiabatic magnetization and vice versa. For $CrCl_3$ the magnetocaloric effect is positive. The dependence is linear in all the cases. The intensity of the magnetic field in these experiments varied from 1000 to 11 000 gauss.

The temperature dependence of the magnetocaloric effect is shown in Fig. 2. Being positive at a temperature above the specific heat jump for $FeCl_2$ and $CoCl_2$, this effect reaches its maximum in the region of the specific heat anomaly and sinking abruptly changes the sign. With further decrease of temperature the magnetocaloric effect decreases and probably undergoes another change of sign below 14°K. This is confirmed by the fact that the magnetocaloric effect in $FeCl_2$ is positive at 14.2°K and $H=5500$ gauss, imperceptible within the accuracy of our measurements at $H=9500$ gauss, and finally, negative at $H=11\,100$ gauss.

From these results it may be inferred that a superposition of two effects of opposite signs takes place in these salts. The positive effect is associated with the orientation of magnetic carriers in the external magnetic field. The negative effect can be accounted for by the increase of the potential energy of the orbital momenta in the electric field of the crystal due to their being forced out of their quenched positions.

The magnetocaloric effect in $CrCl_3$ is positive both below and above the specific heat jump (16.8°K). The probable cause of this difference from the behaviour of the foregoing salts is that, as has been shown by magnetic investigations at low and middle temperatures up to room temperature and by studies of the gyromagnetic effect(4), the only carriers of the magnetic

moment of this salt are the electron spins. It must be assumed that the electric field of a crystal of the anhydrous salt $CrCl_3$ is so strong that ordinary magnetic fields cannot force out the orbits from their quenched position.

Figs. 3 and 4 represent the experimental data on the influence of the external magnetic field on the position of the specific heat jump for $FeCl_2$ and $CoCl_2$. The curves formed by circles represent the heating curves with and

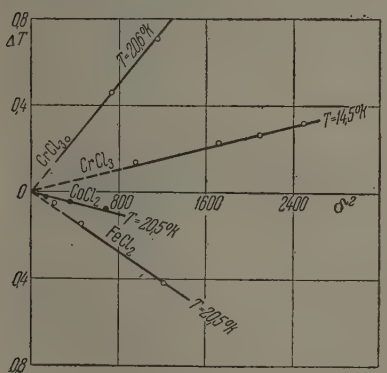

Fig. 1.

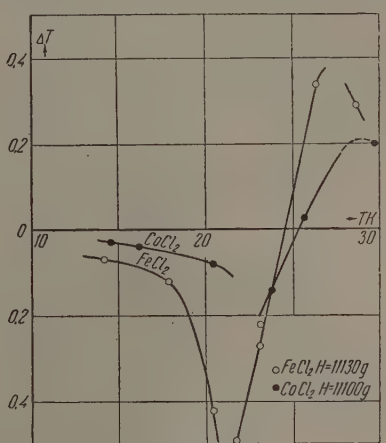

Fig. 2.

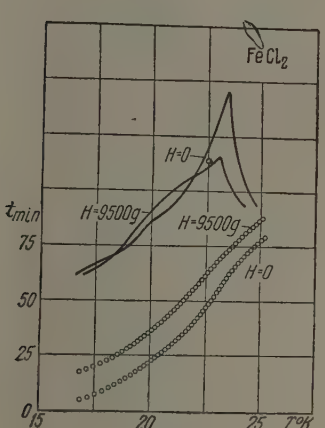

Fig. 3.

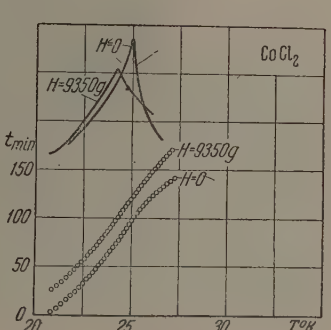

Fig. 4.

without the field. Time is plotted along the axis of ordinates, temperature (under constant heat supply) along the axis of abscissae. The solid curves plotted above them give the dependence of the slope of these curves, i. e. a quantity proportional to the specific heat, on the temperature. As seen from these figures, on applying the magnetic field the specific heat jump in $FeCl_2$ and $CoCl_2$ shifts toward the low temperatures by 0.4°K and 0.7°K, respectively. This fact is likewise in agreement with the hypothesis previously advanced on the nature of the specific heat jump in these salts[3] and makes it impossible to explain this effect by an ordinary transition to ferromagnetic state, as in ferromagnetics the external magnetic field shifts the Curie point towards high temperatures.

In the salt $CrCl_3$ a field of 10 000 gauss does not shift the specific heat jump within 0.1°. The values in the diagrams of the magnetocaloric effect

refer to the whole calorimeter, i. e. to the salt and the material of calorimeter. A measurement of the specific heat of the material of the calorimeter over the temperature region investigated showed it to amount to 5—10% of the total heat capacity. The temperature measurements in our experiments were precise to within 0.01°. The effect of the magnetic field on the resistance of the platinum thermometer was taken into account by a special calibration. The ΔT values are mean values of heating and cooling. As a rule, heating exceeded cooling by 5—10%, which should be referred to the Foucault currents in the metallic parts of the calorimeter and the difference in the specific heat with and without the magnetic field.

At nitrogen temperatures the magnetocaloric effect is not noticeable within the accuracy of our measurements.

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PHYSIK

ULTRAVIOLETTE LUMINESZENZ DER BEI TEMPERATUR DER FLÜSSIGEN LUFT RÖNTGENISIERTEN NaCl-KRISTALLE

Von M. L. KATZ und R. E. SSOLOMONIUK

(Vorgelegt von S. I. Wawilow, Mitglied der Akademie, d. 3. VII. 1939)

Schein und Katz(1) stellten fest, dass plastisch deformierte und undeformierte (getemperte) röntgenisierte NaCl-Kristalle sich verschieden in Bezug auf ultraviolette Luminiszenz verhalten. Das Luminiszenzspektrum undeformierter NaCl-Kristalle besteht im von diesen Verfassern erforschten Spektralgebiete (2 000—3 100 Å) aus einer Bande mit einem Maximum von etwa 235 mμ, während im Luminiszenzspektrum plastisch deformierter Kristalle ausser dieser Bande noch ein verhältnismässig schwaches Leuchten im Gebiet von 290—300 mμ beobachtet wird.

Ein Leuchten im Gebiet der langwelligen Bande (301 mμ) wurde an manchen röntgenisierten NaCl-Kristallen auch von Fedenev(2) beobachtet.

Ein Unterschied in der Luminiszenz plastisch deformierter und undeformierter NaCl-Kristalle wurde im sichtbaren Teile des Spektrums von Urbach(3), Brilliantov and Morgenstern(4) beobachtet. Letztere stellten fest, dass in undeformierten, bei tiefer Temperatur röntgenisierten NaCl-Kristallen zwei Arten von Leuchten auftreten, während in plastisch deformierten drei zur Beobachtung kommen: ein grünes—auch undeformierten Kristallen eigenes, ein blaues, das nur für den deformierten Zustand charakteristisch ist, und ein Nachleuchten. Das Spektrum des blauen Leuchtens ist kontinuierlich und erstreckt sich über den ganzen sichtbaren Teil des Spektrums hinaus bis in das ultraviolette Gebiet ($\lambda = 280$ mμ); es schliesst somit die von Schein und Katz an deformierten, bei Zimmertemperatur röntgenisierten, Kristallen entdeckte Bande ein.

Den Ergebnissen der oben genannten Verfasser widerspricht die Mitteilung von Podaschewskv und Polonsky(5), in der behauptet wird, dass das Luminiszenzspektrum sowohl deformierter, wie auch undeformierter (getemperter) NaCl-Kristalle nur aus einer kurzwelligen Bande bestehe und dass die Deformation, ausser einer Vergrösserung der Leuchtintensität und einer Erweiterung der Bande zum langwelligen Teil des Spektrums hin, keine Veränderungen in der Luminiszenz des Kristalles hervorrufe.

Die in vorliegender Arbeit angeführten Ergebnisse der Erforschung ultravioletter Luminiszenz der bei Temperatur der flüssigen Luft röntgenisierten NaCl-Kristalle bestätigen, ausser allem Übrigen, auch den von vielen Verfassern beobachteten Unterschied im Verhalten der deformierten und undeformierten NaCl-Kristalle.

Es wurde von uns die ultraviolette Luminiszenz von Steinsalzkristallen dreier Gruppen untersucht: 1) natürliche plastisch deformierte, 2) getemper-

te und 3) plastische nach der Temperung deformierte. Die Kristalle wurden auf innere Spannungen nach der optischen Methode kontroliert. Die Messungen wurden mit einem hochempfindlichen Lichtzählrohr mit einer sensibilisierten Platinphotokathode ausgeführt. Die Impulse im Lichtzählrohr wurden durch einen Dreikaskadenverstärker verstärkt und mittels eines elektromagnetischen Zählrelais registriert. Zur Spektralerforschung der Luminiszenz diente ein Zeiss-Monochromator mit Quarzoptik. Die erhaltenen Resultate sind folgende.

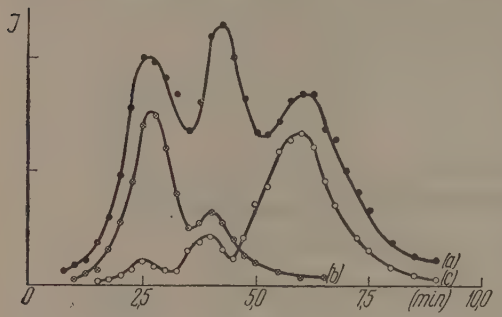

Fig. 1.

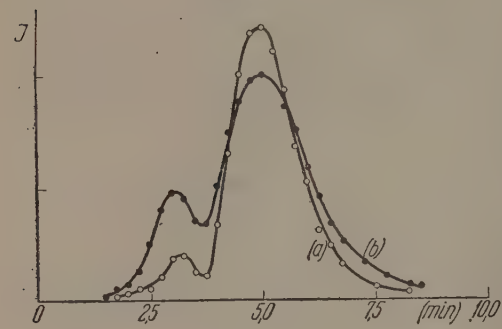

Fig. 2.

1. Die bei Temperatur der flüssigen Luft röntgenisierten NaCl-Kristalle werden viel schwächer verfärbt als diejenigen, welche bei Zimmertemperatur röntgenisiert wurden. Jedoch bei allmählichem Übergehen des Kristalls zur Zimmertemperatur luminisziert er bedeutend intensiver, als wenn er bei Zimmertemperatur röntgenisiert worden wäre.

2. Die Intensitätsveränderung der ultravioletten Luminiszenz bei Temperatur der flüssigen Luft röntgenisierter NaCl-Kristalle verläuft beim natürlichen Erwärmen bis zur Zimmertemperatur bei plastisch deformierten und getemperten Kristallen nicht gleichartig. Die Kurve *a* (Fig. 1) stellt den zeitlichen Intensitätsgang der ultravioletten Luminiszenz in natürlichen plastisch deformierten Kristallen dar. Die Kurve hat drei Helligkeitsmaxima (wir nennen sie weiterhin «Buckel»), die durch bestimmte Temperaturen des allmählich erwärmten Kristalls bedingt werden. Das entsprechende Verhalten eines NaCl-Kristalls, welcher vorher einer dauernden Temperung bei 360°C unterworfen wurde, stellt die Kurve *a* (Fig. 2) dar. Diese Kurve unterscheidet sich von der vorhergehenden durch vollständiges Fehlen des ersten und durch einen verhältnismässig schwach ausgeprägten zweiten Buckel. Die Luminiszenzintensität im dritten Buckel ist um einige Male grösser als in dem entsprechenden Buckel der ungetemperten Kristalle. Bei höheren Temperungstemperaturen (600—700°C) wächst die Luminiszenzintensität im dritten Buckel noch mehr an. Dabei wird die Intensität auch im zweiten Buckel vergrössert, aber das Verhältnis der Gesamtwerte der zu registrierenden Quanten im zweiten und dritten Buckel bleibt hierbei ungefähr dasselbe. Der erste Buckel, welcher den ungetemperten Kristallen eigen ist, entsteht nicht in getemperten unter Einwirkung der plastischen Deformation (Kurve *b* in Fig. 2). Natürliche Kristalle, die keiner speziellen plastischen Deformation unterworfen wurden, verhalten sich im allgemeinen ebenso wie die deformierten, jedoch mit dem Unterschied, dass die oben geschilderten Charaktereigentümlichkeiten weniger deutlich auftreten. In allen Fällen hängt natürlich die Form der Kurven von der Geschwindigkeit der Kristallerwärmung ab.

3. Die Luminiszenzzentren, die den verschiedenen Buckeln der oben angeführten Kurven entsprechen, sind gegen spektral unzerlegtes sichtbares Licht nicht gleich empfindlich. Die Kurve *c* der Fig. 1 ist analog der Kurve *a* derselben Figur erhalten, zwar mit dem Unterschied, dass der Kristall nach der Röntgenisierung binnen drei Minuten in flüssiger Luft durch sichtbares Licht schwacher Intensität bestrahlt wurde. Aus dem Vergleich der Kurven *a* und *c*, die an ein und demselben Kristall erhalten wurden, ist ersichtlich, dass sichtbares Licht viel mehr Wirkung auf die ersten zwei Buckel ausübt als auf den dritten. Bei zehnminutiger Bestrahlung mit sichtbarem Licht verschwinden die ersten zwei Buckel völlig, während der dritte dabei ungefähr um sechs Male geschwächt wird.

4. Mittels eines Filters ist es leicht festzustellen, dass einzelne Buckel der oben angegebenen Kurven zu verschiedenen Spektralbanden gehören. Die Kurven *a* und *b* in Fig. 1 gehören einem und demselben Kristall an, entsprechend erhalten ohne und mit Filter. Nach den Angaben des Filters kann man schliessen, dass jeder nächste Buckel der Kurve einer mehr kurzwelligen Emission entspricht. Ein genaueres Studium der Spektralbeschaffenheit wurde mittels eines Monochromators ausgeführt. Die Kurve *a* in Fig. 3 zeigt, dass die Emission plastisch deformierter (ungetemperter) NaCl-Kristalle aus drei Banden besteht, von denen die kurzwelligste ein Maximum bei 2400 Å, die mittlere etwa bei 3000 Å hat; das Maximum der langwelligen Bande liegt in einem Spektralgebiet, für welches das Platinwasserstoff-Lichtzählrohr unempfindlich ist (das Herstellen der Kurven ist mit Berücksichtigung der Verminderung der Spektralempfindlichkeit des Lichtzählrohrs bei Übergang zu längeren Wellen ausgeführt). In getemperten Kristallen fehlt die langwellige Bande völlig und die mittlere läuft auf verhältnismässig geringe Werte aus (Kurve *b* in Fig. 3). Die Intensität dieser mittleren Bande wächst in einem getemperten Kristall an, wenn der Kristall nach der Temperung einer plastischen Deformation unterworfen wird (Kurve *c* in Fig. 3). Es ist anzunehmen, dass das Vorhandensein dieser Bande in getemperten Kristallen durch Reste innerer Spannungen bedingt ist, von denen es uns nicht gelang uns völlig zu befreien. Merkwürdig ist, dass je langwelliger die Bande, desto tiefer liegt die Temperatur, bei der sie zum Vorschein kommt. Dadurch lässt sich eventuell erklären, dass es bei Zimmertemperatur gelingt bei völligem Fehlen der langwelligsten Bande nur Spuren der mittleren festzustellen. Die von Podaschewsky und Polonskv beschriebene Vergrösserung der Intensität der kurzwelligen Bande unter Einwirkung der plastischen Deformation wurde von uns nicht festgestellt; im Gegenteil, es wurde sogar eine gewisse Verkleinerung beobachtet (Kurve *c* in Fig. 3). Die von diesen Verfassern angeführte einseitige Erweiterung der genannten Bande zum langwelligen Teil des Spektrums hin, unter Einwirkung der plastischen Deformation, wird auch nicht beobachtet.

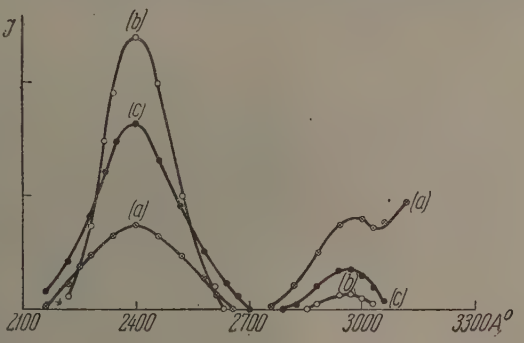

Fig. 3.

Somit zeigt das Obenangeführte deutlich, dass es in deformierten NaCl-Kristallen drei Arten von Luminiszenzzentren gibt, die sich von einander durch Labilität, Aktivierungsenergie und durch die von ihnen bedingten

Spektralbanden unterscheiden. Die Emission der kurzwelligen Bande (2400Å) kann durch den Übergang der Elekronen von den *F*-Zentren entsprechenden Niveaus auf die Grundniveaus gedeutet werden. Das Vorhandensein der mittleren Bande scheint von den durch plastische Deformation hervorgerufene Störungen der Kristallstruktur bedingt zu werden. Die langwelligste Bande, die durch die Temperung irreversibel beseitigt wird, lässt sich wahrscheinlich auf Beimengungen zurückführen, die bei Temperungstemperaturen gewisse chemische Verwandlungen erleiden. Die von uns im ultravioletten und von anderen Verfassern(6) im sichtbaren Teil des Spektrums beobachteten Luminiszenzbanden erweisen, dass die Luminiszenzerscheinungen in röntgenisierten NaCl-Kristallen komplizierter verlaufen, als es nach dem von Tartakowsky(7) vorgeschlagenen Niveauschema zu erwarten war.

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PHYSICS

DETERMINATION OF THE SENSITIVITY OF A PHOTON COUNTER

By I. L. ROICH

(Communicated by S. I. Wawilow, Member of the Academy, 3. VII. 1939)

In investigations concerned with weak intensities of light the photon counter may serve as an important and sometimes unique measuring instrument; this relates in particular to the investigation of optical effects, where the application of the photographic method is difficult. Such, for instance, are investigations of the mytogenetic radiation, of the luminescence of crystals, the study of chemical reactions, and so on.

These investigations imply the knowledge of distribution of spectrum sensitivity, and of absolute sensitivity.

We determined the spectrum sensitivity of a platinum-hydrogen photon counter. For this purpose we used a black body, the radiation from which fell onto a quartz monochromator and thence onto the counter(1). Measurements on the number of impulses of the counter as a function of the wave length were carried out at a constant furnace temperature. The black circles in Fig. 1 correspond to the data obtained by this method. From the law of black body radiation we were able to find the number of light quanta of each wave length, emitted by the furnace; this made it possible to determine the spectrum sensitivity of the counter directly. In Fig. 1 the crosses denote the results which correspond to the theoretical isotherm for the temperature measured, as obtained from the formula for the intensity of radiation from a black body:

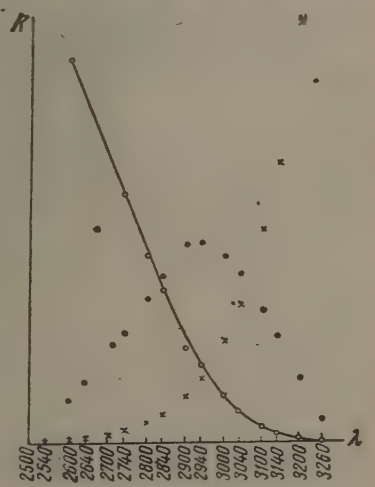

Fig. 1.

$$E_{\lambda T} = \frac{c_1}{\lambda^5} \frac{1}{e^{\frac{c_2}{\lambda T}} - 1}.$$

By dividing the experimental values by respective values from the theoretical isotherm we obtain the curve of spectrum sensitivity (denoted by circles).

It is of great interest to determine the sensitivity of the counter in absolute units. The method usually suggested consists in that a light intensity measured by a thermoelement is weakened to such an extent as to make it capable of being measured with a photon counter. Owing to the great sensitivity of the counters, it is necessary to weaken the light intensity very considerably ($10^5 \div 10^8$ times), thus introducing considerable error. To these should be added errors introduced in the case when ultraviolet radiation is measured with a thermoelement.

The method suggested by us consists in that as the source of light we use a black body; the energy radiated from it can be applied to determine the absolute sensitivity of the counter. We have already pointed out the possibility of making accurate measurements of very weak ultraviolet radiation emitted by a black body within the temperature range of 1513—17530°K. It was shown that the radiation from such a source follows the law of black body radiation. It is therefore possible to use this source for absolute measurements and for the calculation of the number of light quanta of a definite wave length emitted by our black body.

We set ourselves the problem of determining the absolute sensitivity of a platinum-hydrogen photon counter. A definite amount of energy of black body radiation fell onto the slit of a quartz monochromator. A definite wave length was chosen after suitable spectral resolution. The light beam was concentrated on the counter and accurate measurements of the number of impulses were made. A special device employing a second quartz monochromator was used to determine the absorption of the first one.

The calculations were carried out on the following basis. It is known that the amount of energy radiated by a black body is:

$$G = E_{\lambda, T}\, d\lambda\, df\, d\omega\, dt$$

where $E_{\lambda,T}$ is the intensity of radiation from the black body, $d\lambda$—the range of wave lengths, df—the area of the aperture of the black body, $d\omega$—the solid angle, dt—the time.

The results of the measurements show that at a temperature of 1753° and a wave length of 3000 Å the photon counter recorded 63 impulses per minute.

In order to calculate the limit sensitivity, the number of dark impulses has to be taken into account. During the whole period of operation the number of dark impulses showed an average of 2.1 per minute.

We are thus able to make reliable measurements of the light flux which releases 0.5 photoelectrons per minute. To measure so weak a radiation, the experiment must be carried out for a certain definite time.

Let n be the number of dark impulses and t the time in minutes, then it is still possible to observe the number of impulses per minute m of a light of unknown intensity, if, taking into account the statistics(²) of oscillations, we obtain:

$$\sqrt{tn} \leqslant tm - \left|\sqrt{t(m+n)}\right|;$$

thus, putting 2.1 in place of n, 0.5 in place of m, we find t=36 min.

Hence we find the limit sensitivity of the platinum-hydrogen photon counter; in the given case for 3000 Å it is 128 quanta/cm² sec. We can also calculate the limit sensitivity for other wave lengths from the curve of spectrum sensitivity.

We calculated the sensitivity for 3200, 3140, 3100, 2800, 2640 and 2600 Å. In order to calculate the sensitivity below 2600 Å we proceeded from the probable extrapolation of the spectrum sensitivity curve (the spectrum

sensitivity curve is given in Fig. 2, the dotted line showing the probable extrapolation below 2600 Å).

From this latter part of the curve we calculated the limit sensitivities of the counter for 2540, 2300, 2100 and 2000 Å. The results obtained are summarized in the table.

Å	Quanta / cm² sec
3 200	1 979
3 140	641
3 100	334
3 000	128
2 640	14.3
2 540	10.3
2 300	5.4
2 100	4
2 000	3

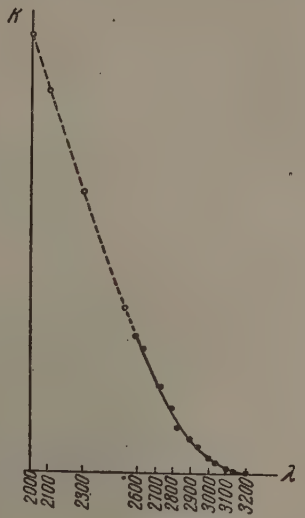

Fig. 2.

The left-hand column of the table gives the wave length in Ångstrom units, and the right-hand column the corresponding value of the limit sensitivity in quanta per cm² per second.

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PHYSIQUE

ABSORPTION DES ONDES ULTRA-ACOUSTIQUES DANS UN MÉLANGE ACÉTONE—EAU

Par P. A. BAJOULINE et J. M. MERSON

(Présenté par L. I. Mandelstam, de l'Académie, le 29. VI. 1939)

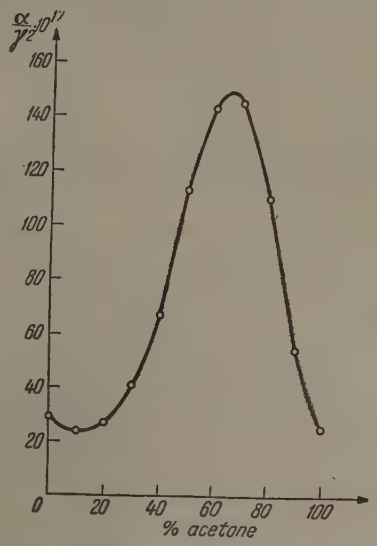
Dans la présente Note sont donnés les résultats préliminaires des mesures de l'absorption des ondes ultra-acoustiques par le système acétone—eau pour les différentes fréquences et concentrations. L'étude était effectuée dans l'intervalle de fréquences de 19 000 jusqu'à 3800 kHz. La méthode des mesures etait basée sur un phénomène connu de diffraction de la lumière sur les ondes ultra-acoustiques. La description détaillée de cette méthode est donnée dans l'article de P. A. Bajouline(1).

Le tableau donne les résultats des mesures du coefficient d'absorption α par le système acétone—eau en fonction de la fréquence et de la concentration. α désigne le coefficient d'absorption pour l'amplitude de cm^{-1}. La concentration est donnée en volumes (le rapport en tre le du volume d'un des composants et le volume total). Pendant l'expérience la température variait de 16.5 à 19.5° C.

Teneur de l'acétone dans l'eau, %	38 000 kHz		29 500 kHz		26 000 kHz		19 000 kHz		$\alpha/\nu^2 \cdot 10^{17}$ valeur moyenne	$\alpha/\nu^2 \cdot 10^{17}$ valeur calculée, $t = 23°C$
	α	$\alpha/\nu^2 \cdot 10^{17}$	α	$\alpha/\nu^2 \cdot 10^{17}$	α	$\alpha/\nu^2 \cdot 10^{17}$	α	$\alpha/\nu^2 \cdot 10^{17}$		
0	0.42	29	0.25	29	0.19	28	—	—	29	7.1
10	0.37	26	0.20	23	0.16	24	—	—	24	7.6
20	0.38	26	0.23	26	0.19	28	—	—	27	8.2
30	0.59	41	0.38	44	0.26	39	—	—	41	8.9
40	0.99	69	0.58	67	0.44	65	0.25	69	67	9.8
50	1.42	98	1.03	118	0.89	132	0.37	103	113	—
60	—	—	1.22	140	1.01	149	0.51	141	143	10.4
70	—	—	1.19	137	0.96	142	0.56	155	145	—
80	—	—	0.89	102	0.69	102	0.45	125	110	9.3
90	0.75	52	0.51	59	0.34	50	—	—	54	—
100	0.35	24	0.23	26	0.17	25	—	—	25	6.5

Ou voit sur la figure la dépendance de α/ν^2 de la concentration. La valeur de α/ν^2 est moyenne de toutes les mesures pour la concentration donnée. Comme on le voit dans le tableau, la valeur de α dépend probablement de la fréquence suivant la loi quadratique, et si cette loi n'est pas justifiée pour toutes les concentrations, néanmoins les écarts n'ont pas un caractère systématique et sont probablement dus au hasard. On voit du tableau et de la figure que pour le mélange en question le coefficient d'absorption pour toutes les frequences a un maximum très marqué aux environs de 60—70%

de teneur de l'acétone. Pour cette concentration de l'acétone la valeur de α/ν^2 devient six fois plus grande par rapport à nos composants. Les diminutions de la valeur de α dans le domaine des petites concentrations de l'acétone, quoique systématiques pour toutes les fréquences étudiées, ne peuvent servir tout de même de base pour des conclusions quelconques, car ces diminutions de valeur de α sont inférieures aux erreurs possibles de l'expérience.



Il est intéressant de noter qu'en confrontant les données expérimentales au résultats calculés par la formule de Stokes et en ne tenant compte que du coefficient ordinaire de viscosité, nous trouvons de même le maximum pour la teneur 60—70% de l'acétone.

Nous avons également effectué des mesures de l'absorption pour les différentes températures, le mélange ayant la teneur en acétone 70%, dans l'intervalle de 20—38° C. Les mesures ont montrées que le coefficient d'absorption décroît lorsque la température augmente. Les mesures pour les températures plus élevées ont été difficiles à rèaliser vu la présence des flux thermiques.

Notons que pour les systèmes tels que benzène—toluène, ether—CCl_4 et autres ([1],[2]), où α de l'un des composants est considérablement plus grand que celui de l'autre, la dépendance de l'absorption de la concentration est telle que le coefficient d'absorption décroît rapidement avec la concentration. Mais, par contre, dans le système acétone—eau le coefficient d'absorption de l'un et de l'autre composants est à peu près le même; or, la fonction de la concentration possède un maximum très marqué.

D'autres faits expérimentaux indiquent que le système en question a encore des maxima pour les valeurs des autres propriétés en fonction de la concentration. Ainsi, les mesures effectuées par P. Prosoroff ont montrées que la vitesse de l'ultra-son a un maximum pour la teneur en acétone dans l'eau de 30%. La viscosité du système a un maximum pour la concentration voisine de 40% de l'acétone.

Il est intéressant d'observer que l'étude en rayons X montre que le système en question n'est pas homogène, c'est-à-dire que dans les petites régions a lieu la répartition inégale des molécules. De plus, la même étude a montrée que le caractère de l'hétérogénéité dépend aussi de la concentration.

Ce phénomène permet de supposer que dans notre système peut avoir lieu l'absorption supplémentaire due à l'effet relaxial sur ses hétérogénéités.

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BIOPHYSICS

INSTANTANEOUS VISUAL THRESHOLD AFTER LIGHT ADAPTATION

By N. T. FEDOROV and V. I. FEDOROVA

(Communicated by S. I. Wawilow, Member of the Academy, 23. VI. 1939)

The exposure of the retina of the eye to light leads to a very complex process in our optic apparatus. First of all, in the retina there set in some photochemical changes and appear certain decomposition products of the light sensitive substance which call forth some impulses in the optic nerve. Being modified to a certain extent in the synapses, these impulses reach the visual centers of the brain where they produce one or another visual sensation. The intensity of this sensation depends on the sensitivity of the brain which in its turn is determined by a number of factors.

The biochemical aspect of the first stage of the process of vision has been greatly elucidated within the recent time by Wald's investigations([1]) on the most important pigment of the retina, i. e. the visual purple (rhodopsine). From this author's data it follows that: 1) the visual purple is formed in the retina from the vitamin A; 2) that it breaks under the action of light into two molecules, viz. a molecule of retinene (this corresponds to what has been previously called the «visual yellow») and a molecule of protein. Concurrently with the decomposition of the visual purple there proceed two reactions: part of the molecules of retinene combine with the protein molecules forming again the visual purple, while another part are converted into colourless products, thus compensating for the loss of vitamin A. Despite the complex character of this scheme, a number of events associated with vision may be described quantitatively with the aid of two additional assumptions which are by themselves most plausible. It may be assumed in fact together with Wald that the reverse reaction is of a bimolecular order, or, as suggested, e. g., by Lazareff and Haschek, that it is monomolecular. The attempts to decide between these two alternatives by following the course of dark adaptation proved futile, since the kinetics of dark adaptation after a prolonged preliminary illumination of the eye are largely determined by the rate of restitution of the light sensitive substance from vitamin A, but not from the decomposition products of rhodopsine ([2]). Wehave attempted, therefore, to decide this question by analyzing the experimental data reported by Blanchard ([3]) for the initial sensitivity of the eye after adaptation to brightnesses varying within the range of 10^{-7} to 10^{2} milliambert, i. e. 10^{9} times. Blanchard's experiments consisted in cutting off the light as soon as the adaptation of the eye to a given brightness by looking at a large suitably illuminated area is achieved. After this there was determined the threshold brightness of a 5° area, at which the latter becomes visible instantaneously upon switching out the adapting light. These experiments were made with «white» light and red, yellow, green and blue regions of the spectrum isolated by means of narrow filters. The initial threshold was found to rise with increase in illumination of the screen ser-

ving for preliminary adaptation. This increase is approximately similar for all the colours at medium and high intensities, while at small intensities it is different.

The following is the physical-chemical scheme of these experiments. Upon exposure to light reflected from a screen whose intensity we shall designate as I, in the retina there are formed decomposition products of the light sensitive substance which stimulate the nerve endings; let their concentration be x. The rate of formation of these photoproducts conforms to:

$$\frac{dx}{dt} = k\frac{s}{h\nu}(1 - e^{-\varepsilon(X-x)}) - k_2 x^n \tag{1}$$

where k and k_2 are constants, X is the initial concentration, and n is equal to 1 or 2. For small $\varepsilon(X-x)$ we obtain from the equation (1):

$$\frac{dx}{dt} = k\frac{\varepsilon I}{h\nu}(X - x).$$

But since the brightness $B = \alpha\frac{\varepsilon I}{h\nu}X$ [cf. (4), p. 76], we may write

$$\frac{dx}{dt} = k_1 B_a(1 - x_0') - k_2 x_0^n = k_1 B_a(1 - x_0') - k_2' x_0'^n \tag{2}$$

where $x_0' = \frac{x_0}{X}$. Assuming that the preliminary light adaptation practically resulted in establishing a stationary state and that the rate of increase of x approaches zero, we may write

$$k_1 B_a(1 - x_0') = k_2' x_0'^n \tag{2'}$$

whence we can find x_0':

$$x_0' = \frac{k' B_a}{1 + k' B_a}, \tag{3}$$

where $k' = \frac{k_1}{k_2}$ for $n = 1$ and

$$x_0' = \frac{1}{2}[(k'^2 B_a^2 + 4k' B_a)^{\frac{1}{2}} - k' B_a]. \tag{4}$$

Hereupon the light was shut off and the threshold B_t instantaneously determined. The equilibrium will be obviously disturbed and equation (2) will now run as follows:

$$-\frac{d(X-x)}{dt} = \frac{dx}{dt} = k_1 B_t(1 - x_0' - x') - k_2 x^n - k_3' x_0'. \tag{5}$$ *

Its integral for $n = 1$ and for the initial condition: $x = 0$ for $t = 0$, taken for a small initial time interval τ, when we can content ourselves with the first member with the first power of τ, will be as follows

$$\Delta x = [k_1 B_t(1 - x_0') - k_3' x_0']\tau; \tag{6}$$

hence, assuming that for the threshold sensation Δx equals a certain constant value A whose magnitude depends on the sensitivity of the brain, we shall obtain the following value of the initial threshold:

$$B_t = \frac{\frac{A}{\tau} + k_3' x_0'}{k_1(1 - x_0')} = k\frac{b + x_0'}{1 - x_0'}. \tag{7}$$

[The same formula may be derived in another way. It follows from equation (5) that for the initial time moment $t = 0$: $\left(\frac{dx}{dt}\right)_{t=0} = k_1 B_t(1 - x_0') - k_3' x_0'$, whence for a very small initial time interval τ the formula (7) is valid]. Substituting x_0' from equation (3) we have

$$B_t = \alpha + \beta B_a, \text{ where } \alpha \text{ and } \beta \text{ are constant.} \tag{8}$$

* This equation is derived in a way similar to equation (5) of the article by N. T. Fedorov in C. R. Acad. Sci. URSS, XXIV, No. 7 (1939).

Thus, in the case of a monomolecular reverse reaction the initial threshold is a linear function of the light intensity, to which the eye has been previously adapted.

The integration of equation (5) for the case $n=2$ and for a small t gives a similar expression for Δx:

$$\Delta x = [k_1 B_t (1 - x_0') - k_3 x_0'] \tau. \qquad (6')$$

On the assumption that for the threshold Δx equals a constant value A', we obtain analogically to equation (7)

$$B_t = \frac{\frac{A}{\tau} + k_3 x_0'}{k_1 (1 - x_0')} = k' \frac{b + x_0'}{1 - x_0'}. \qquad (9)$$

Substituting x', we ultimately obtain

$$B_t = k' \frac{b + \frac{1}{2}\left[(k'^2 B_a^2 + 4k' B_a)^{\frac{1}{2}} - k' B_a\right]}{1 - \frac{1}{2}\left[(k'^2 B_b^2 + 4k' B_a)^{\frac{1}{2}} - k' B_a\right]}. \qquad (10)$$

Equations (8) and (10) imply a relationship between the initial threshold and brightness to which the eye has previously been adapted; this relationship is accessible to experimental control. To compare formulae (9) and (10) with Blanchard's experimental data two corrections should be introduced which give the illumination of the retina, since it is certainly only these illuminations that determine the kinetics of the process called forth by light. The first correction for the pupil area (Blanchard experimented with the natural pupil) can be readily done, since Blanchard has determined the diameter of the pupil of his eye within a wide range of variations of brightness. The second correction which makes allowance for the dissimilarity in the efficiency of rays falling at different distances from the center of the pupil (the effect of Stiles and Crawford) has been introduced as follows.

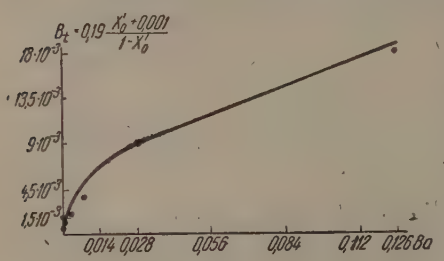

Fig. 1.

Stiles and Crawford* present only graphs for three subjects illustrating the correlation between the log of this correlation (log E) and the area of the pupil. This correlation proves linear, and since the slopes of the straight lines practically coincide, we were able to determine log E for the pupil area in question having recourse to such an «average straight line». The total correction was therefore obtained by multiplying the area of the pupil by E. In the table we present numerical values of log E calculated for various pupil areas which are always to be introduced when determining the luminosity of the retina (in the case of central fixation) together with the correction for the pupil area.

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* Stiles and Crawford (5) offer a table of corrections for various values of brightness of the screen; however, this table cannot be taken use of, as it is based on the values of the Rieves' pupil.

Since the determinations of the threshold are made at the moment when the illumination of the screen is switched out, one has to take for B_t the

Pupil area in mm²	log E
43.0	$\bar{1}$.740
42.9	$\bar{1}$.742
42.8	$\bar{1}$.743
42.7	$\bar{1}$.744
42.2	$\bar{1}$.748
41.3	$\bar{1}$.752
40.2	$\bar{1}$.760
38.3	$\bar{1}$.772
34.8	$\bar{1}$.792
28.0	$\bar{1}$.836
16.9	$\bar{1}$.904
11.3	$\bar{1}$.940
6.8	$\bar{1}$.966
4.1	$\bar{1}$.983
3.2	$\bar{1}$.988

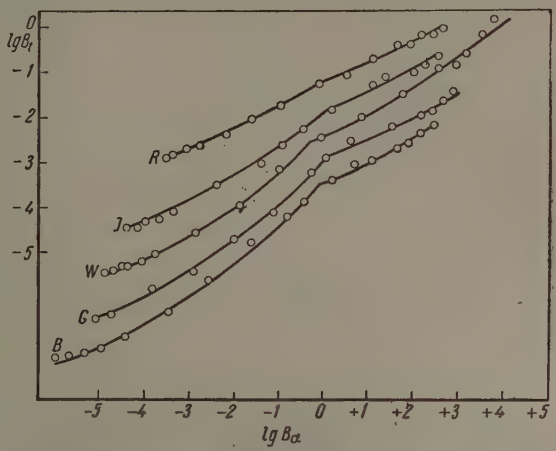

Fig. 2. Figures plotted along the ordinate refer to curve R. Each subsequent is replaced downward with regard to the preceding one by 0.5 log unit.

same corrections as for B_a. The results of these calculations are represented in Fig. 1 and 2 by dots and circles, while the solid line illustrates the values derived from formula (10). It will be seen from Fig. 1 and 2 that: 1) $n=1$ when the relationship between B_t and B_a is linear [cf. formula (9)], does not agree with the experiment; 2) $n=2$ gives a very good agreement between theory and experiment within the variation range of B_a 10^{-8} times; and 3) all the curves break into two sections which correspond to the rod and cone functions. As, however, in Blanchard's experiments the field's size was 5°, a reproduction of this work both for the foveal (with a field-size more than 1.4°) and the peripheral vision, involving the application of the artificial pupil, is very advisable. In concluding it should be pointed out that a different photochemical approach to Blanchard's data was made by Hecht[6] who concluded that equation (1) should be written as follows:

$$\frac{dx}{dt} = k_1 B_a (1-x)^2 - k_2 x^2.$$

This conclusion is based on an assumption which does not seem correct, viz. that at the first moment after the completion of light adaptation upon exposure to a threshold brightness B_t the rate $\frac{dx}{dt}$ is expressed by the equation

$$\left(\frac{dx}{dt}\right)_{t=0} = k_1 B_t (1-x_0)^n$$

[cf. equation (7) of our article]. Moreover, Hecht has introduced a somewhat different correction for the effect of Stiles and Crawford which we failed to make consistent with the data of these authors.

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BIOPHYSICS

THEORY OF THE EYE'S PHOTOMETRIC SENSITIVITY

By N. T. FEDOROV

(Communicated by S. I. Wawilow, Member of the Academy, 27. VI. 1939)

It was as early as in 1865 that the German physiologist Aubert (1) made his first precise quantitative measurements of the variation in visual intensity discrimination with the intensity I. The visual intensity discrimination has been since frequently called the contrast sensitivity, while we gave it the name of the photometric sensitivity of the eye, defining it as the reciprocal of $\frac{\Delta I}{I}$, where I is the intensity. 25 years later König and Brodhun (2) have made measurements of this relationship over a wider range of intensities both for the «white» light and six monochromatic regions of the spectrum. 28 years thereupon a similar study was carried out by Blanchard (3) who was followed by Holladay, Lowry (4), Houstoun (5) and, lastly, by J. Steinhardt (6) and Hecht, Peskin and Patt (7).

Without dwelling upon any of these works separately (a review of them can be found in S. Hecht's book «La base chimique et structurelle de la vision», 1938, Paris), it will only be mentioned that they reveal quite a definite and characteristic relationship between $\frac{\Delta I}{I}$ and $\log I$ which may be found in all the textbooks on optics and physiology and varies only in details (presence or absence of an increase of $\frac{\Delta I}{I}$ with greater brightnesses, size of field of vision, conditions of adaptation, etc.).

The first attempt to interpret the facts established by König and Brodhun was made by Helmholtz (8) who endeavoured to modify Weber-Fechner's law $\frac{\Delta I}{I+\beta}=\Delta E$, so as to obtain a faithful description of the data reported by König and Brodhun. He found it necessary to assume that the value β, termed by Fechner the «self-light of the retina», varied in magnitude from one retinal element to another. If this be the case, the Weber-Fechner law should be read as follows:

$$dE = dI \int_0^{\alpha} \frac{\varphi d\alpha}{I+\alpha} \qquad (1)$$

where $\varphi d\alpha$ is the area of the retinal elements whose «self-light» varies from α to $\alpha+d\alpha$, while the integral is taken for the entire area of the retina where the «self-light» varies from 0 to α. While faithfully reproducing the course of the function $\frac{\Delta I}{I}$, formula (1) is however but a formal mathematical

description of the results of some processes not accounted for by Helmholtz' theory. P. P. Lazareff ([9],[10]) was the first to approach the intermediate link between the stimulus and the sensation, i. e. the stimulation. We adhere to Cobb's hypothesis ([11]), according to which a merely perceptible difference in brightness necessarily implies the decomposition of a certain constant amount of light sensitive substance. This hypothesis was further developed by Hecht ([12]) who discarded it later on, being unable to reconciliate it with the experimental evidence available. Instead he advanced the hypothesis ([13]) that no perceptible difference in brightness can be obtained, unless the initial rate of decomposition of the light sensitive substance upon addition of ΔI is the same, whatever the intensity I may be.

The application of this theory to the experimental data obtained for the human eye gave satisfactory results, although it seems hardly plausible both photochemically and biochemically that the rate of the primary photochemical reaction in the light sensitive substance of the retina is proportional to the square of the available concentration of this substance, as postulated by this theory. Moreover, the latter fails to account for the results recently obtained by Graham and Kamp ([14]) who found quite definite a correlation between $\frac{\Delta I}{I}$ and the duration of presentation of ΔI which in their experiments varied within the range of 0.002 to 0.5 sec., whereas according to Hecht's theory $\frac{\Delta I}{I}$ should not depend upon the time of presentation.

Our theory which assumes: 1) Cobb's hypothesis, 2) the monomolecular order of the photochemical reaction, 3) the bimolecular order of the reverse reaction (c. f. C. R. Acad. Sci. URSS, this issue) and 4) a visual cycle analogous to the scheme of Wald, offers the possibility to account for the bulk of the experimental evidence actually available, as well as for the new experimental data obtained in this laboratory by Plakhov for the fields of about 1.20' in size. This theory is as follows.

When the retina is exposed to light I, the rate of formation of the substance stimulating the nerve endings is

$$\frac{dx}{dt} = k\frac{I}{h\nu}(1 - e^{-\varepsilon(X-x)}) - k_2X^2. \qquad (2)$$

For cones in which the concentration of the light sensitive substance should be thousands times less than in rods, by expressing $e^{-\varepsilon(X-x)}$ in terms of infinite series with increasing powers of $\varepsilon(X-x)$, the second member of this series will be infinitesimal so that the equation (1) may be written as follows:

$$\frac{dx}{dt} = k_1I(X-x) - k_2X^2. \qquad (3)$$

As to the rods, it is held by Wald that at the maximum of absorption (close to 500 mμ), $\varepsilon(X-x)$ is approximately 0.12. Hence, if we neglect the members with $\varepsilon(X-x)$ in powers higher than unity, our error will not exceed 5% for 500 mμ and be less than 5% for all the other wave lengths. The same order of magnitude will be obtained according to other authors as well.

As both in the present and in the subsequent communications we confine ourselves only to cone vision, the substitution of equation (2) by equation (3) will necessarily result in but infinitesimal errors. The solution of equation (3) for the stationary state ($t = \infty$) gives:

$$x_0 = \frac{2X}{1+\beta} \qquad (4)$$

where $\beta = \sqrt{1 + \frac{4b}{B_0}}$; $b = \frac{k_2 X^2 a}{k_1}$, and brightness $B_0 = \alpha \frac{\varepsilon I}{h\nu} X$ or, which is the same,

$$x_0 = \frac{X}{2}\left[(b_1^2 B^2 + 4 b_1 B)^{\frac{1}{2}} - b_1 B\right] \qquad (4')$$

where $b_1 = \frac{X}{b}$ *.

Let us increase for a short time, after the stationary state is attained, the light intensity of the one half of the field by ΔI which corresponds to a merely perceptible increment in brightness. The rate of decrease in the supply of the light sensitive substance will be determined by the difference between the rate of the direct photochemical reaction which is proportional to ΔI and the amount of the light sensitive substance available, as well as by the rate of the reverse bimolecular reaction and that of restitution of the light sensitive substance, which we assume to be proportional to the difference between the maximum amount of the light sensitive substance X and its amount available $x' = X - x_0$, i. e. proportional to x_0. Algebraically we obtain:

$$-\frac{d(X-x)}{dt} = \frac{dx}{dt} = k_1 \Delta I (X - x_0 - x) - k_2 x^2 - k_3 x_0. \qquad (5)$$

The integral of this equation taken for the initial, small time interval τ, equals

$$\Delta x = \tau [k_1 \Delta I (X - x_0) - k_3 x_0]. \qquad (5')$$

Assuming that even a scarcely perceptible difference in the brightness cannot be obtained unless Δx equals a certain constant value α', we have

$$k_1 \Delta I (X - x_0) = \frac{\alpha'}{\tau} + k_3 x_0. \qquad (6)$$

Dividing equation (6) by the equation for stationary state $k_1 I (X - x) = k_2 x^2$, we have

$$\frac{\Delta I}{I} = \frac{\alpha'}{\tau k_2 x_0^2} + \frac{k_3}{k_2 x_0} = \frac{\alpha}{\tau x_0^2} + \frac{\beta}{x_0}. \qquad (7)\ **$$

Substituting for x_0 its value from equation (4) for different B, we represent $\frac{\Delta I}{I}$ as a function of B or I.

However, in those cases when ΔI was presented not during a short time interval τ, but continuously (in Graham and Cobb's experiments, for $\tau > 0.08$ sec.), $\frac{\Delta I}{I}$ proves independent of the presentation time ΔI, which should be taken to mean that during this interval of time a stationary state has been established in the retina:

$$k_1 \Delta I (X - x_0 - \Delta x) = k_2 \Delta x^2 + k_3 x_0. \qquad (8)$$

From equations (8) and (4) we derive

$$\frac{\Delta I}{I} - \frac{\Delta I}{I} \cdot \frac{\Delta x}{X - x_0} = \frac{\alpha}{x_0^2} + \frac{\beta}{x_0}. \qquad (9)$$

This equation (9) transforms into an equation of type (7) provided $\frac{\Delta x}{X - x_0}$ is a small fraction, that is to say, if within the range of the common brightnesses the increment Δx which is indispensable for obtaining a just percep-

* Cf. N. T. Fedorov and V. I. Fedorova, C. R. Acad. Sci. URSS, XXII, No. 2 (1939).

** As $\frac{\Delta I}{I}$ is identical with $\frac{\Delta B}{B}$, we can obviously replace it with $\frac{\Delta B}{B}$ throughout the expression.

tible difference in brightness between two adjacent fields, is small as compared to the amount of non-decomposed substance $X-x_0$. Our experiments show that within a very wide range of brightnesses the function of $\frac{\Delta I}{I}$ on I is determined by equation (9) without the member $\frac{\Delta x}{X-x_0}$, i. e. by equation

$$\frac{\Delta I}{I}=\frac{\alpha_1}{x_0^2}+\frac{\beta}{x_0} \qquad (10)$$

which also points to the fact that the value Δx is actually a very small fraction of X. Further on it follows from our theory which postulates the existence in the eye of only two light sensitive substances, one for the rods and another for the cones, that at similar brightnesses $\frac{\Delta I}{I}$ must not depend on the colour. As a matter of fact, Plakhov's experiments show that this is the case when I is changed up to 55 000 times. This yields an additional argument in favour of our hypothesis (cf. our publication in collaboration with V. I. Fedorova) as to the number of light sensitive substances in the retina.

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PHOTOMETRIC SENSITIVITY OF THE EYE

By N. T. FEDOROV and V. I. FEDOROVA

(Communicated by S. I. Wawilow, Member of the Academy, 27. VI. 1939)

In a previous communication (1) one of us has advanced a general theo of the mechanism of photometric sensitivity of the eye.

The formulae (7) and (9) developed in this publication which conne the photometric sensitivity of the eye with the brightness of the stimul

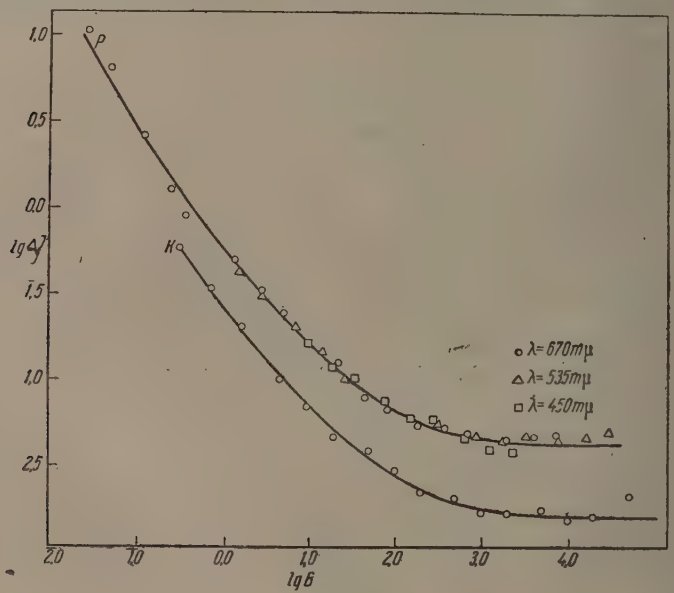

Fig. 1.

and the time of its presentation, have been applied by us to the experime tal data of König and Brodhun (for red light), to those of Hecht, Pes and Patt, Graham and Kamp, Steinhardt, and lastly to data obtai in this laboratory by A. Plakhov.

In Fig. 1 the experimental data of König and Brodhun for the spect red light ($\lambda = 670$ mμ) for König's eye are represented by circles, while t solid line has been derived from our formula

$$\frac{\Delta I}{I} = \frac{0.0155}{x_0'} + \frac{0.000816}{x_0'^2}; \quad b = 115.$$

The data of Hecht, Peskin and Patt are plotted as circles (red light, subject P.); the dominant wave length $\lambda = 670$ mμ. The solid line has been computed from our formula

$$\frac{\Delta I}{I} = \frac{0.0406}{x_0'} + \frac{0.00214}{x_0'^2}; \quad b = 83.3$$

As mentioned by the above authors, the cone sections of their curves somewhat diverge for different colours; however, they consider this as an artifact presumably due to the possible variation in the shutter of their device, by means of which ΔI was presented for 0.04 sec. throughout an investigation that lasted several months. This is why by the end of the study they have on the same day determined the maximum value of $\frac{\Delta I}{I}$ for great intensities of different colours.

It follows from these measurements that $\frac{\Delta I}{I}$ is similar for all the colours tested, the maximum discrepancy amounting approximately to 10%. If this is the case, the curves should coincide when shifted along the ordinate, which actually takes place, as may be seen from Fig. 1, where the triangles and squares showing the data obtained for green ($\lambda = 535$ mμ) and blue light ($\lambda = 450$ mμ) are somewhat displaced along the ordinate. The data for rod vision fit in as well, provided their respective constants are used.

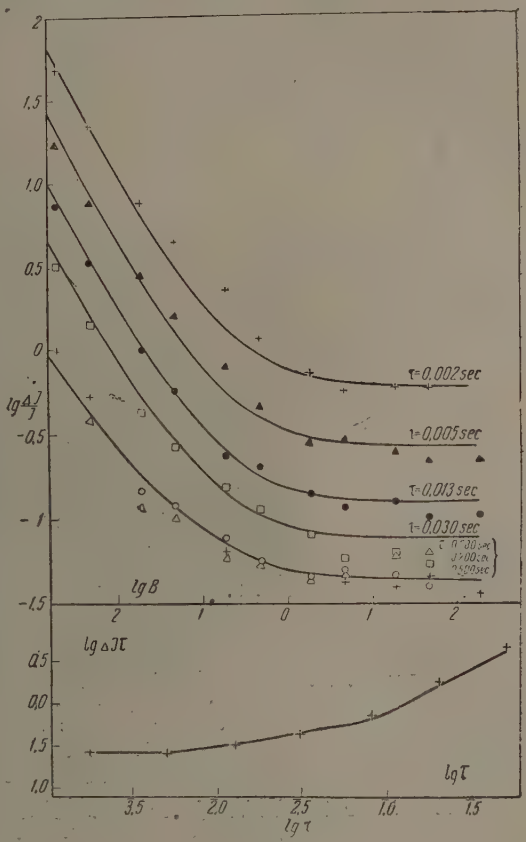

Fig. 2.

Fig. 2 illustrates Graham and Kamp's values of $\frac{\Delta I}{I}$ for a duration of exposure of ΔI varying from 0.002 to 0.5 sec. Taking into account that the errors involved in the determination of ΔI for small duration τ are sure to be very considerable, it will be seen that all these curves conform to our formula, the value of $\frac{\Delta I}{I}$ for τ less than 0.08 being as follows:

$$\frac{\Delta I}{I} = \frac{0.038}{x_0'} + \frac{0.00115}{\tau x_0'^2}; \quad b = 6.80$$

while for τ greater than 0.08 it is expressed by the formula for stationary state:

$$\frac{\Delta I}{I} = \frac{0.038}{x_0'} + \frac{0.005}{x_0'^2}; \quad b = 6.80.$$

At the bottom of Fig. 2 we have plotted the values of $\log \Delta I\tau$ as a function of $\log \tau$ for $\log B = 1.67$, the solid line having been calculated theoretically and the experimental data being shown by crosses. All the other B values exhibit a similar character; in almost all of them the points for the time 0.08 sec. fail to fit in completely, which seems to be due to the stationary state not yet established. Nevertheless, we cannot take the integral of the differential equation (5) for $\tau = 0.08$ in the form of (5′).

Without dwelling upon Steinhardt's data which conform to our formulae, nor on those of König, Brodhun, Hecht, Peskin and Patt, we shall proceed to the study of the relationship between $\frac{\Delta I}{I}$ and B for pointed heterochromatic stimuli (0.1 mm at a distance of 27.5 cm, which corresponds to the angle 1.25′). This investigation was carried out in our laboratory under the author's guidance by Plakhov with the help of the following device.

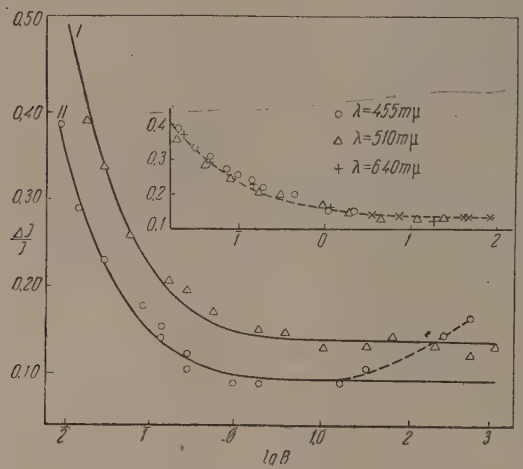

Fig. 3.

The radiation of a source of light (a 1000 W kinoprojection cylindrical lamp of the Mazda type, or, in one series, a pointolite lamp) was collected by means of a lens on mat glass. Immediately behind it a black metal plate with a 0.1 mm hole was placed. In front of the hole there was mounted a Rochon prism which doubles the image of the hole in such a way that it can be drawn nearer to or removed from the plate with the hole, thus altering the distance between the luminous points. These were examined through a polarization prism of the Frank-Ritter type, situated in front of the eye behind an artificial pupil. The rotation angle of the prism was determined with an accuracy of one tenth of grade. In order to change B, a set of grey filters accurately measured throughout the spectrum were used, by means of which the brightness could be changed 55 000 times. After matching the polarizer was rotated until just a perceptible difference was obtained, and $\frac{\Delta I}{I}$ was determined by the angles of rotation in the first and second case. For white light two curves were obtained whose experimental points are the averages of 2—3 series of experiments carried out on different days. Each separate point was computed from 20—30 readings. One of these curves, obtained for such a distance between the points that the interval between them disappeared only at the greatest brightness, is given in Fig. 3, I, respective numerical values being summarized in the table. The second curve obtained for a distance between points, at which they fused already at medium brightness, is shown in Fig. 3, II; respective data are summarized in the 3rd and 4th columns of the table.

It may be seen from the data obtained that beginning with the brightness B, at which no interval could be noticed between the points, curve of $\frac{\Delta I}{I}$ is rising with the increase of $\log I$. From our point of view this is to

B_1 (in lux on white)	$\left(\frac{\Delta I}{I}\right)_I$	B_2	$\left(\frac{\Delta I}{I}\right)_{II}$
1 000	0.130	—	—
500	0.120	500	0.164
—	—	250	0.143
205	0.129	—	—
65	0.141	—	—
32.5	0.130	32.5	0.105
10.25	0.129	16.25	0.088
3.63	0.142	5.12	0.088
1.82	0.150	0.91	0.088
0.54	0.170	0.27	0.104; 0.122
0.27	0.195	0.135	0.154; 0.140
0.166	0.208	0.083	0.177
0.0585	0.262	0.0292	0.238; 0.230
0.0293	0.337	0.0146	0.290
0.0184	0.390	0.0092	0.386

be accounted for by the fact that owing to irradiation a much greater Δx is required in this case for discrimination of the difference of brightnesses, so that we cannot disregard in formula (9) the member with $\frac{\Delta x}{X - x_0}$, whose presence makes such a rise inevitable.

The solid lines in Fig. 3 are derived from our formulae

$$\frac{\Delta I}{I} = \frac{0.1293}{x_0'} + \frac{0.068}{x_0'^2} \text{ and } \frac{\Delta I}{I} = \frac{0.0864}{x_0'} + \frac{0.00454}{x_0'^2}; \quad b = 0.0912.$$

With chromatic points the measurements were taken with red, green and blue light-filters with accurately controlled spectral transparency. In this way their dominant wave lengths were determined to be $\lambda_1 = 640$ mμ, $\lambda_2 = 510$ mμ and $\lambda_3 = 455$ mμ respectively, for the source A (2842°). The total transparency coefficient was computed after the energy distribution of a 1000 W lamp had been measured by matching it spectrometrically with a control lamp, as well as with the curve of spectral sensitivity for the experimenter's eye. The numerical values of these coefficients proved to be

$$T_{red} = 0.0825; \; T_{green} = 0.0218 \text{ and } T_{blue} = 0.00218, \text{ respectively.}$$

With these figures on hand I could be expressed in units similar for all the colours and proportional to the brightness of the points B. The results obtained with the chromatic points are illustrated by Fig. 3. At the top of this figure it may be seen that within the accuracy of measurements the change of $\frac{\Delta I}{I}$ as a function of B does not depend on the colour. This would not be the case if several light sensitive substances were present in the retina.

Thus, the theory developed in the present communication enables us to quantitatively interpret all the evidence available, as well as the new experimental data on the relationship between the photometric sensitivity of the eye and brightness.

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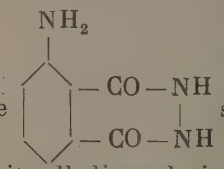
PHYSICAL CHEMISTRY

CHEMILUMINESCENCE OF 3-AMINO-PHTALHYDRAZIDE (LUMINOL)

By E. S. WASSERMANN

(Communicated by S. I. Wawilow, Member of the Academy, 8. VI. 1939)

It is known that 3-amino-phtalhydrazide  shows a brilliant chemiluminescence at the oxidation of its alkaline solutions by hydrogen peroxide in the presence of promotors, such as are hypochlorite, potassium ferricyanide or preparations containing the haematin-complex (haemin, haemoglobin and others)(1).

The glow of luminol is noticeable even in the case of dilute solutions and with very small concentrations of above-mentioned substances.

Different authors tested the catalytic action of various cations upon the glow of luminol in oxidizing it by means of hydrogen peroxide. It was noticed that copper excites a strong but a very short flash. It was also pointed out that salts of metals which decompose catalytic hydrogen peroxide, Fe^{III}, Mn^{II}, Co^{II}, give also a short flash(2). Closer examination of the action of various catalysts has shown that of many tested metals there are but little that give a strong and durable increasing of glow. The ferric, manganese salts (Fe^{III} and Mn^{II}) give only a weak and short flash*. Nickel salts did not react at all. Cobalt (Co^{II}) gives the strongest and the most durable effect, and a more feeble effect gives copper. Cobalt shows, however, its maximum influence only at certain conditions, namely at certain pH of medium and in the presence of ions of $CO_3^{=}$.

3-amino-pthalhydrazide [synthesized after Huntress and al.(5) and Drew and Pearman(6)] was employed for this investigation. There was prepared a solution of luminol 0.003 g-mol. in 1 l of water in which 0.003 g-mol. Na_2CO_3 was dissolved. Thus, a nearly neutral solution of luminol was obtained, each cm³ containing $3 \cdot 10^{-6}$ g-mol. Five cm³ of this solution ($1 \cdot 5.10^{-5}$ g-mol.) were placed in a beaker and added with 10 cm³ of a buffer solution adjusted to a certain pH, 2 cm³ of cobalt salt [$Co(NO_3)_2$] dissolved to 0.002 g-mol in 1 l ($4 \cdot 10^{-6}$ g-mol.) and a solution of 2 cm³ 0.9% H_2O_2 ($1 \cdot 10^{-3}$ g-mol.). As the latter was added, the start of luminescence was reccorded with a stop-watch.

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* A strong glow gives iron bound into a complex with cyanide salts, e. g. with $K_3Fe(CN)_6$, haemin complex, salicylic aldehyde aethylen-diamin complex(3) and phtalicyanin complex(4).

One minute later the deflection of a beam of light from the mirror-galvanometer was measured. The latter was connected with a selen photoelectric cell placed in a dark camera with the light of the shining liquid falling upon it. The proportions of acting substances used were as follows: luminol (hydrogen peroxide) catalyst=3.75 : 250 : 1, i. e. 66 g-mol. H_2O_2 and 0.26 g-mol. catalyst

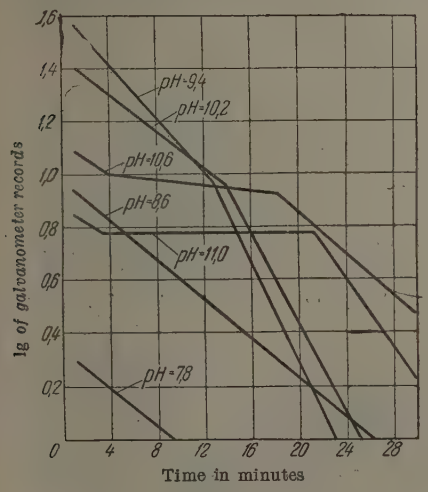

Fig. 1.

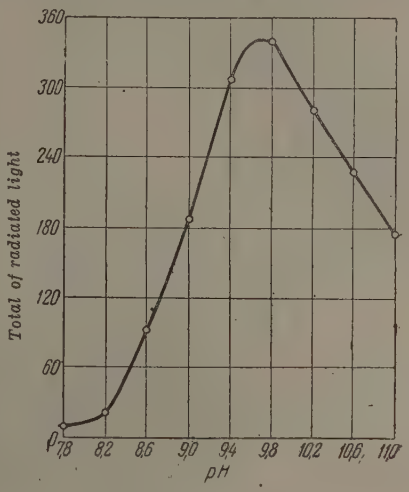

Fig. 2.

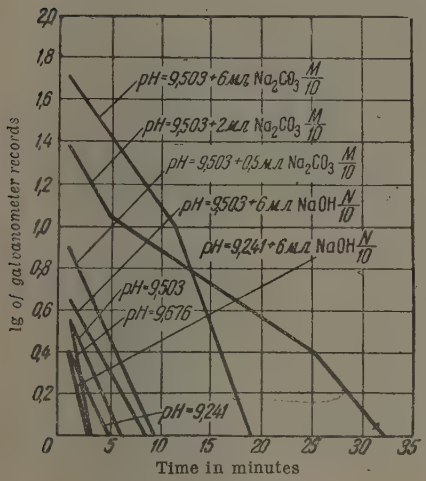

Fig. 3.

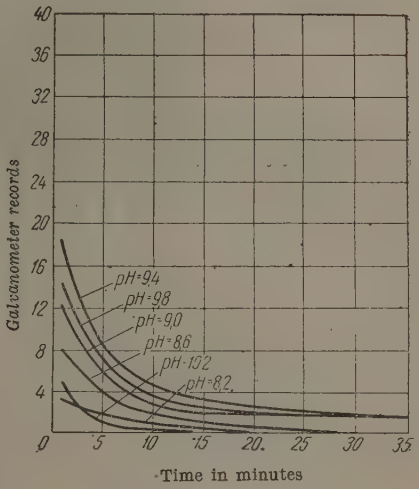

Fig. 4.

were taken up by 1 molecule of luminol. Atkins and Pantin's bufferic mixture was employed containing: 1) 0.1 g-mol. H_3BO_3 and 0.1 g-mol. KCl in 1 l, and 2) 0.1 g-mol. Na_2CO_3 in 1 l. In Fig. 1 the power and duration of the luminescence in arbitrary deflection units of a galvanometer (sensibility $0.4 \cdot 10^{-9}$ A on 1° a 1 m distance) placed at a distance of 1.6 m from the screen, is plotted against various pH obtained by means of above-mentioned bufferic mixtures. In Fig. 2 the ordinate represents instead of deflection values their logarithma (Fig. 1 and 2). The curves take the shape of steep down straight lines. As

it is seen from the figures, luminiscence begins only at pH above 8, the intensity is a maximum at pH=9.4—9.8, decreasing with the rising of the pH. An interesting point to note here is that with pH=10.6—11 the decreasing of intensity is delayed and we have a long glow, governed by some different laws, compared to those which act with other pH of the medium. If the intensity of light (in galvanometer readings) is multiplied by time (in minutes), we obtain the sum of light ΣI. In Fig. 3 the change of ΣI with the pH of the medium is shown (at buffers containing soda).

Furthermore, instead of bufferic mixtures consisting of sodium carbonate and boric acid Sorensen's bufferic mixtures were taken: 1) 0.2 g-mol. H_3BO_3+0.1 g-mol. NaOH in 1 l, and 2) 0.1 *n* NaOH. It turned out that at different pH with those bufferic solutions the luminescence showed a very weak intensity. The addition of soda caused an abrupt rise in intensity (Fig. 4). That this increase in intensity may not be explained by pH having increased through addition of soda, is obvious from the fact that the addition of an equivalent amount of sodium hydroxide failed to give any noticeable raising of intensity, and that $NaHCO_3$ increased the luminescence equally as Na_2CO_3.

Thus, the luminescence of aminophtalhydrazide in the presence of a promotor (cobalt) is sensitive to the presence of carbonate ions. If the ions of carbonic acid were substituted for oxalic or for acetic acid ions, cobalt refused increase the luminescence. The specificity of cobalt (Co^{II}; Co^{III} acts very weakly) is to be emphasized here. Copper, though it activates the luminescence, acts much more weakly than Co^{II}. Fig. 4 shows the luminescence of luminol in the presence of Cu^{II} at soda buffers.

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CHEMISTRY

DISTRIBUTION OF BORON BETWEEN LIQUID AND SOLID PHASES OF THE INDER LAKE BRINES DURING ISOTHERMAL EVAPORATION

By I. N. LEPESHKOV and A. I. SHPIKELMAN

(Communicated by N. S. Kurnakov, Member of the Academy, 28. VI. 1939)

The Inder salt lake lies 160 km north of Guriew (Western Kazakhstan) and covers an area of about 110 km². The presence of a vast salt dome underlying the lake was established by geochemical investigations and bore-hole surveying made in the Inder district.

The brines of Inder lake contain large amounts of salts of potassium, boron, bromine, etc. (Table 1).

The enrichment of the lake brines with the above-mentioned salts is in progress at the expense of the salt deposits of the dome through washing out of the latter by the numerous springs flowing into the lake.

The physical-chemical investigations carried out by the Institute of General and Inorganic Chemistry(1) have demonstrated that the brines of Inder lake are similar (at 28.5° Bé conc.) with the solutions obtained by lixiviation of the Solikamsk potassium salts(2). This fact is another witness in favour of the conjecture made by N. S. Kurnakov about the analogy and connexion existing between the Ural-Emba and Solikamsk salt deposits. Later on, the discovery of boron in the Inder district attracted even greater attention to the investigation of the Inder lake brines and to the possibility of their manysided utilization in obtaining the salts of potassium, bromine, boron, magnesium, etc.

In the present paper we have brought forward some data on the content of boron in the Inder lake brines and on its distribution in the liquid and solid phases of the latter during the isothermal evaporation.

The evaporation of the brines was carried out at 25°C. A method of direct titration by the alkali with the addition of mannite was used by the authors for the determination of boron. The results of the determinations of boron in the liquid and solid phases of the Inder brines at the concentrations from 26 to 39° Bé are given in Table 2.

It will be obvious from the data obtained that the amount of boron in the Inder lake brine increases with the concentration of the latter coming up to 0.9% of B_2O_3 at 39° Bé conc. of the brine.

In has been pointed out in a paper by V. I. Nikolaev and S. K. Kosman on the content of boric acid in the brines of Chokrak Lake(3) that the concentration of boron may be increased by strengthening the brine, but not beyond the point at which magnesium sulphate starts settling, since, according to their data, the boron is then precipitated too, owing to a metathetical reac-

Table 1

Chemical Analysis of the Inder Lake Brine at a 24° Bé Conc.

Salts	Weight %	Coefficient of metamorphism $MgSO_4/MgCl_2$
$Ca(HCO_3)_2$	0.054	0.1
$CaSO_4$	0.258	
$MgSO_4$	0.435	
KCl	1.945	
NaCl	19.88	
$MgCl_2$	4.081	
Total	26.654	
B_2O_3 (at 26° Bé)	0.102	
Br (at 28.5° Bé)	0.310	

Table 2

Content of Boron in the Liquid and Solid Phases during the Isothermal Evaporation of the Inder Lake Brines

	Liquid phase	Solid phase
Conc. in the Bé degrees	Weight % of B_2O_3	Weight % of B_2O_3
26.0	0.102	None
26.5	0.135	»
27.0	0.142	»
27.5	0.162	»
29.5	0.300	»
30.0	0.370	0.0059
33.0	0.480	None
34.0	0.57	»
35.0	0.61	»
36.0	0.69	»
37.0	0.74	0.12
38.0	0.80	»
39.0	0.90	»

tion between borax and magnesium salts. Besides, some of the brine with the boron in it is carried away by the precipitated crystals of magnesium sulphate. According to N. S. Kurnakov and V. I. Nikolaev, the precipitated crystals of $MgSO_4 . 6H_2O$ are capable of holding up to 15% of the brine.

The magnesium sulphates do not deposit in the solid phase from the potassium salt brines of the Inder lake, but accumulate almost to the eutonics on account of the low content of the former in these brines. Hence it is clear that during the evaporation of the brine the percentage of boron in the latter will increase with the increase of concentration of the brine. The presence of trifling amounts of boron in the solid phase is to be accounted for by the brine being not perfectly expressed from the crystals.

The data obtained by the authors on the accumulation of boron in the brine during evaporation have a practical interest from the standpoint of a complex utilization of the Inder brine and manufacture of boron.

The great importance for the national economy of the utilization of the Inder lake brines with an aim of obtaining the salts of potassium, bromine, etc. was pointed out at the All-Union Conference for Potassium and Boron, organized by the Institute of General and Inorganic Chemistry jointly with Glavchimprom in April 1939.

The possibilities of complex utilization of the Inder lake brines will be explored in the current year along with the geochemical investigations to be made in the Inder district.

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CHEMISTRY

INVESTIGATION OF INTER-SOLVATE EXCHANGE OF BROMINE IONS IN VARIOUS SOLVENTS

By S. Z. ROGINSKI, Corresponding Member of the Academy, and V. E. TARTAKOVSKAJA

It is owing to the application of radioactive halogens as indicators in studying the precipitation of halogeneous salts of silver from the mixed alcohol-aqueous solutions, that we have been able to discover an unequal rate of precipitation of halogen iones, which before the mixing were in a purely aqueous or purely alcohol solution([1]).

This effect has been observed with alkali salts of chlorine, bromine and iodine and was manifest in an unequal activity of the precipitations, obtained in a successive precipitation of a few different portions of halogen ions by silver nitrate. This effect has a purely kinetic character and disappears on prolonged heating of the mixture before the precipitation and under the action of a catalyst [acid([1],[2],[3])].

In order to explain the phenomenon discovered, it is necessary to assume that the microscopic mixing and uniform distribution of the anions do not take place instantly and can lag strongly behind the macroscopic one. Owing to this the halogen ions which have been in pure alcohol and in pure water preserve for a while, even after the mixing, different solvate envelopes. This difference disappears through inter-solvate exchange accelerated by the increase of the temperature and introduction of a catalyst.

The preservation in a solution of ions with different solvate envelopes becomes apparent through the action of certain reagents which are able to react in various directions or with various velocity with water and alcohol solvates.

Accordingly, the conditions for the effect observed to appear are as follows: 1) The presence of a retardation in the uniform distributions of the dissolved substances between the solvates (slowness of the inter-solvate exchange); 2) the presence of substances which react in different ways with solvate ions of the two types; 3) the slowness of the isotopic exchange between the product of the reaction mentioned in 2 and the initial substance in solution.

If the interpretation is correct, the detailed investigation of the effect discovered can play an essential rôle in the elucidation of the structure of solutions and of the character of processes, proceeding in mixed solutions. It was therefore interesting to examine the extent of generality of the phenomenon in respect to various solvents.

For this purpose the precipitation of bromine ions from a number of mixed solvents has been investigated which has shown that the retardation

of inter-solvate exchange presents by no means a specific feature of the ethanol-aqueous mixtures, being also observed in a number of other systems. The choice of solvents was limited by the condition of a good solubility of halogen salts in both solvents in their pure state.

As in the preceding papers on the inter-solvate exchange([2]), the experimental method was as follows:

1. Two portions of a halogen salt were prepared, one of them without and the other with a radioactive isotope*.

2. Each of the two portions was dissolved in the corresponding solvent (which was a component of the system under consideration).

3. Four portions of a silver nitrate solution of a definite concentration were taken and the solution was slightly acidified by nitric acid. The amount of silver in all the portions was equivalent to the total contents of the halogen in the solution.

4. A series of successive precipitations was carried out. The precipitates were rapidly filtrated, washed with water, dried up and covered with a protecting collodion layer, after which with the help of a Geiger counter the relative contents of radioactive halogen in these precipitates was measured.

With the help of this method 12 binary solvents (table) have been investigated.

NaBr is Precipitated from a Mixed Solvent

Mixed solvent	Difference in the activity of the precipitation	Note
Ethyl alcohol—water	+ Observed	In all cases nearly saturated salt solutions were mixed
Acetone—water	+ »	
Glycerine—water	+ »	
Glycerine—acetone	+ »	
Methyl alcohol—water	+ »	
Ethyl alcohol—butyl alc.	— Not detected	
Ethyl alcohol—amyl alc.	— » »	
Ethyl alcohol—methyl alc.	— » »	
Ethyl alcohol—glycerine	— » »	
Ethyl alcohol—acetone	— » »	
Methyl alcohol—butyl alc.	— » »	
Amyl alcohol—methyl alc.	— » »	
Methyl alcohol—acetone	— » »	

As is clear from the table, the effect of the lag in the inter-solvate exchange can be observed for the systems: 1) ethanol—water, 2) acetone—water, 3) glycerine—water, 4) glycerine—acetone, 5) methyl alcohol—water. Mixtures of the members of the same homologous series give no effect. Nor is the latter attained if ethyl alcohol with acetone, methyl alcohol with acetone and ethyl alcohol with glycerine are mixed.

As a rule, the experiments were carried out with highly concentrated solutions; only in investigating the system ethyl alcohol—water have we used varying concentrations of the salt (NaBr) and of the precipitate ($AgNO_3$).

The activity of the successive precipitates remains variable within a wide range of concentrations of the precipitator $AgNO_3$—from 30 till 7%—and with the transition to alcohol solutions of the same salt. Positive results, too, are obtained in the case of the precipitation of a 0.1 solution of Hg^{++}_2 ions.

* In this paper, as in all the preceding works, the neutron irradiation of the preparations was carried out in the State Radium Institute, which kindly offered to us this possibility.

The successive precipitates decreased in activity at a constant rate which varied, however, with the conditions of the experiments, especially with the relative amounts of the two pure solutions, from 5 to 1.5. In all the cases the bromine introduced before mixing into the water solution prevailed in the first precipitates of the halogen salts (AgBr, Hg_2Br_2), while the alcohol bromine prevailed in the last precipitates. The prevailing of water bromine in the precipitates is also observed in the water—glycerine, water—acetone and water—methanol. In the mixtures of glycerine with acetone the glycerine bromine is precipitated first. If pure ethyl alcohol is replaced by the water—alcohol as one of the initial solvents, the inequality of the activities of the precipitates is preserved until the content of water in alcohol is nearly 40% and disappears if it is higher.

These data and a number of other kinetic observations on the magnitude and the stability of the effect point to the existence, under the conditions of macroscopic equilibrium in mixed solutions, of solvates containing molecules of one of the solvents only in the envelope surrounding the ions. We incline to the opinion that a similar structure of solvates occurs also in some mixed solvents which show no anomaly of the above type in the precipitation with Ag^+ ions, but that in these cases the difference in the precipitation rates of AgBr is not sufficiently large.

Let us summarize our information about the new effect which is established on the stability of individual solvents in the solutions.

1. The effect is observed with all the three halogen ions investigated: Cl^-, Br^- and I^-.
2. In five mixed solvents (table).
3. As reagent Ag^+, Hg_2^{++} proved to be effective.
4. The effect has a purely kinetic character and disappears if the solution is kept a sufficiently long time at room temperature before the precipitation.
5. The velocity of disappearence is different for different systems.
6. The rise in temperature and the addition of acids to the solution lowers the period, during which the solution is able to a preferred precipitation of the ions of a certain origin.
7. The succession in the precipitations of halogen ions of a certain origin remains always the same.

We are thus entitled to say that the longevity of individual solvates in mixed solvents and the slowness of the inter-solvate exchange is not a specific property of the solvates of halogen ions in water—alcohol solutions, but is observed in a number of other systems.

The next object of experimental attacks is the question whether the existence of such stable solvates is possible in the case of cations and whether there may be a delay in the establishment of physical constants in the solutions on mixing. The theory of this phenomenon will be treated in a special paper.

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AGROCHEMISTRY

GROWTH AND QUALITY OF SUGAR-BEET ROOT AS INFLUENCED BY PERIODICAL SUPPLY OF NITROGEN AND POTASSIUM

By I. V. GULIAKIN

(Communicated by D. N. Prianishnikov, Member of the Academy, 21. VII. 1939)

Some vegetation experiments with sand and soil cultures carried on by the author in the year 1936 had for object to ascertain the behaviour of sugar beet in response to varying rations of nitrogen and potassium supplied at various periods of growth. The sand culture was essentially the Hellriegel's nutrient mixture modified according to the plan of the experiment.

In varying the supply with regard to the elements tested we took account of the fact that the aerial organs and the root of the beet grow at different periods. The aerial organs form during the first period and their total weight is a maximum at the end of July or early in August, while the root grows continuously with the maximum increase in August. The change of the nutrient mixture was effected by washing the culture vessels with tap water and distilled water until no nitrogen could be detected by reaction and then the nutrient mixture respectively modified was introduced.

Table 1

No. of set	Ratio in Hellriegel's mixture of				Average weight of root in g	Sugar content in %	Amount of sugar per root in g	Non-protein of nitrogen root in %	Conventional yield of sugar per root in g
	Nitrogen		Potassium						
	before Aug. 1	after Aug. 1	before Aug. 1	after Aug. 1					
1	4	4	2	2	209.0	14.9	31.1	0.304	15.2
2	4	1/2	2	2	242.0	15.3	37.0	0.175	26.4
3	1/2	4	2	2	89.3	12.4	11.9	0.394	3.1
4	4	4	4	4	244.3	15.0	36.6	0.346	15.5
5	4	1/2	4	4	366.0	17.6	64.4	0.107	54.6
6	4	1/2	1/4	4	71.3	14.7	10.5	0.113	8.5

The evidence furnished by the experiment of 1936 (Table 1) is that root weight is strongly reduced if nitrogen was deficient when the aerial organs were forming (set 3). This deleterious effect cannot be repaired by increasing the supply of nitrogen during the later time. Favourable results were obtained with a liberal supply of nitrogen during the first period and its reduction during the second period (sets 3 and 5). Decreasing the ratio of nitrogen in the

supply 8 times when root growth and sugar storage were very intensive resulted in the root having increased in weight and quality. The positive effect was still more pronounced if the plant was liberally supplied with potassium: then the increase in weight was 49.8%, in sugar content 2.6%, while the content of non-protein nitrogen was three times lower (sets 4 and 5). With a poor supply of potassium, however, the effect of reducing the nitrogen was to increase the weight of the root only by 15.8%, the sugar content by 0.4% , and the content of protein nitrogen was only two times lower (sets 1 and 2). Growth differences between the plants of the above sets were not considerable at the time preceding the change of the nutrient mixture (before August 1) (Table 2). This may be taken to mean that the double ratio of potassium in Hellriegel's mixture was quite sufficient.

Table 2

Ratio of nitrogen	Ratio of potassium	June 25			August 1		
		Weight of a plant in g	Weight of aerial organs in g	Weight of root in g	Weight of a plant in g	Weight of aerial organs in g	Weight of root in g
4	2	19.0	17.6	1.4	193.4	126.1	67.3
4	4	15.7	14.6	1.1	237.0	157.0	80.0

A growing leaf is a strong absorber of nitrogen ([2],[3],[4]). High amounts of this element are therefore absorbed and assimilated by the aboveground part of a sugar-beet while it is forming. Accordingly, it is during this period that the plant requires the greatest quantity of nitrogen in the nutrient medium.

When intensive root growth and sugar storage are taking place, the need for nitrogen is considerably reduced. If the sugar-beet is given less nitrogen at that time, the protein breakdown in the ageing leaf is accelerated. Unless this acceleration exceeds a certain limit, it has a positive effect on the root yield. With too rapid a breakdown of proteins, however, the leaves die away before time and the eventual decrease in root weight is the result.

Table 3

No. of set	Ratio in Hellriegel's mixture of				Average weight of root in g	Sugar content in %	Amount of sugar per root in g	Non-protein nitrogen in root in %	Conventional yield of sugar per root in g
	Nitrogen		Potassium						
	before Aug. 1	after Aug. 1	before Aug. 1	after Aug. 1					
1	4	4	4	4	744	18.3	132.2	0.304	79.7
2	4	4	4	1/2	762	15.8	110.5	0.334	46.8
3	4	1/2	4	1/2	563	18.4	103.6	0.165	80.4
4	4	1/2	4	4	606	20.4	123.6	0.229	89.0
5	4	4	1/2	4	562	13.2	74.1	0.331	27.7
6	4	1/2	1/2	4	258	23.6	60.9	0.172	60.0

This phenomenon was actually observed in the experiment of 1937 (Table 3). Here, too strong a decrease of nitrogen in the supply brought about a decrease in the root weight (sets 1 and 4). This was because part of the ageing leaves, most valuable with regard to root growth and sugar storage, died away all too soon after being formed during June and July. But though the

root decreased in weight considerably, its sugar content was nearly the same and the conventional yield of sugar was even higher.

Therefore, in order to obtain a high yield of good quality root in the sugar-beet, we have to create conditions which will make for vigorous growth of aerial organs during the early development of the plant in June and the first half of July. One of those indispensable conditions is an intensive supply of nitrogen to the plant at that time. During the period of enhanced accumulation of sugars the supply of nitrogen must be reduced. Its rôle is then only to preserve from decay the assimilation apparatus created during June—July and keep it in a condition of physiological ripeness (ageing) and good working capacity.

Not only is the supply of nitrogen a positive factor during leaf growth, but the supply of potassium is also of great importance. If potassium is deficient at that time, the root weight is eventually reduced (set 6, Table 1; sets 5 and 6, Table 3), and so is also the quality of the root, which is dependent on the ratio of N to K in the supply (set 5, Table 3). But contrary to what had been stated with respect to nitrogen, the intensive supply of potassium to the sugar-beet must be continued over a longer period, since it is an important factor not only in leaf formation, but also in root growth and sugar accumulation. If potassium is deficient during this latter period, the root will decrease both in weight and quality (sets 2 and 3, Table 3). However, the positive influence of a liberal supply of potassium during sugar accumulation will not come into play unless the supply of nitrogen is reduced (sets 4 and 5, Table 1; sets 5 and 6, Table 3). An adequate ratio of N to K in the nutrition of sugar-beet must be adjusted both during leaf growth and sugar accumulation, but it is adequate if it is higher during the first than the second of those periods, whereby the supply of potassium must be kept at a continuously high level and it is the supply of nitrogen which has to decrease. In order to obtain as high a yield of sugar-beet as 500—600 centners per ha, the nitrogen must be supplied liberally and its considerable amounts will certainly remain in the soil during sugar accumulation, when it is no longer needed in such a high proportion, and its excessive quantity acts only unfavourably upon the yield. To control the supply of nitrogen in practice is therefore a matter of considerable difficulty, especially if its decrease is required. One of the possible means to do this is to bound the mineral forms of nitrogen biologically by increasing the life activity of microorganisms through introduction into the soil of organic substances which contain no or very little nitrogen and will quickly decompose there. Thus, in the vegetation experiment of 1938 with soil cultures the quality of the beet root was increased by a mixture of starch and sucrose being introduced into the culture solution (Table 4).

Table 4

No. of set	Experimental plan: Vessels filled with	Introduced on Aug. 1 per vessel in g: Starch	Sucrose	P_2O_5	Average weight of root in g	Sugar content in %	Amount of sugar per root in g	Non-protein nitrogen in root in %	Conventional yield of sugar per root in g
1	Soil +	—	—	—	553	16.70	92.2	0.131	74.1
2	4g N	15	15	—	624	17.4	108.3	0.069	97.5
3	2.5g P_2O_5	15	15	1.5	554	17.7	98.1	0.092	85.4
4	7.5g K_2O per vessel	—	—	1.5	462	18.9	87.3	0.107	74.9

From these data it is evident that here the introduction of organic matter deprived of nitrogen was analogous in its influence on the yield of root to the reduction of nitrogen employed in the previous experiments. In field conditions similar effect may possibly be achieved by using straw with a wide ratio of C to N.

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GENETICS

ON NATURAL SELECTION IN POPULATIONS

By S. J. KRAJEVOJ

(Communicated by N. I. Vavilov, Member of the Academy, 13. VI. 1939)

In the present paper we have communicated data on the examination of the vital resistance and biological fitness of mutant in barley obtained by treating young ears with X-rays.

As a material for the work served mutations obtained by means of X-raying young ears of *Hordeum sativum* var. *medicum* Körn., 046. This is a distichous smooth-awned barley, bred at the Odessa Agricultural Experimental Station (D. I. Baransky). On the photograph are represented the mutants and the original form from which they were obtained. *A*—the initial form *H. s.* var. *medicum* Körn., 046. *Б*—a mutant obtained from the initial form (*A*) named by us *H. s.* var *triaristatum*, since its broad (3 mm) spikelet glumae bear rather long awns, the length of which attains that of the ear, so that the spikelet has 3 awns (two of them on the spikelet gluma and the third on the flower gluma). *B*—mutant obtained from the initial form (*A*) named by us *H. s.* var. *compactum*; it has a considerably condensed ear as compared to the initial form (*A*). *Г*—mutant similarly obtained from the initial form (*A*) named by us *H. s.* var. *Pismenkovi* in honour of the experimentator who has obtained all the mutants we worked with, F. A. Pismenko. This mutant shows at the base of the ear a characteristically curved stem like a cork-driver (see the photograph). *Д*—mutant obtained in the same way as all the preceding ones from the original form (*A*). It has very thin (underdeveloped) short awns which nearly fall off during ripening, so that the ear assumes the appearance represented in the photograph (*Д*). It should be noted that this was a weak, sickly plant of very low productivity. We have named it *H. s.* var. *nonaristatum*. Lastly, there was one mutant included into the trial; it is not represented in the photograph and named by us *H. s.* var. *fistulosum*. This mutant has a peculiar characteristic consisting in the fact that, instead of normal leaves, tubular leaves, like those in onion, are developed owing to coalescence

of the edges of the leaf blade; the next leaf pierces this tube through, etc., until the ear appears with great difficulty, similarly through a torn tubular leaf. This mutant is also of low productivity, since the tubular leaves check the development of the plant.

All the mutant enumerated above were tried under various eco-geographical conditions in population. Simple and complex populations were prepared. Simple populations consisted only of two components, the initial form and one of the above-mentioned mutants. Complex populations consisted of the initial form and all the remaining mutants obtained from it (table).

As may be seen from the table, the simple populations were prepared in such a way as to make them contain equal number of plants of the two kinds, i. e. equal numbers of kernels of the initial form and of the mutant (50%+ +50%) were taken; then they were mixed together, thoroughly stirred and sown. There were taken 200, 150, 100 and 50 kernels. In parantheses (table) stands the number of kernels planted, before the parentheses, the number of plants obtained from the kernels sown.

The complex population was made in such a manner as to make it contain all the mutants together with the initial form and, besides, in a definite relation (table). Sowing was planned so as to make the area of nutrition of individual plants equal in all the simple and complex populations.

At the beginning it was planned to conduct these experiments at three eco-geograhical regions of the USSR (Khibiny, 67° 40′ N. l.; Moscow, 55°45′ N. l.; Kherson, 46° 40′ N. l.), but owing to certain circumstances, it could not be done. The experiment was conducted mainly in Moscow and, in part, at Odessa.

It is of interest what is the dynamics of elimination of mutant forms in simple and compound populations. The data of 1937 on simple and compound populations obtained in Moscow showed that some of the mutants do better in a compound population, others, on the contrary. Thus, for example, the mutant *H. s.* var. *triaristatum* was eliminated in a compound population in 6.7%, whereas the same mutant was eliminated for 18% in a simple population. The mutant *H. s.* var. *compactum* in a compound population was eliminated only in 4%, in a simple one in 16%. There are opposite examples; thus, the mutant *H. s.* var. *fistulosum* in a compound population was eliminated in 50%, whereas only 24% of its individuals were eliminated in a simple population.

In 1938 the experiment was conducted only in Moscow. The second generation from the one of the compound and two simple populations was grown. Not all the seeds obtained from plants grown in 1937 were sown in 1938, but there was taken a definite fraction of the plants belonging to each component (in proportion to the number of plants of each component).

If we compare the data on simple population of 1938 with those of 1937, it will be seen that in 1937 (when the populations were started) the elimination of the mutant forms was considerably lower than in 1938. This phenomenon may be accounted for by the fact that in 1937 the initial form and the mutants were present in populations in equal numbers, whereas in 1938 the relation was strikingly changed; owing to considerable elimination of mutants in the first generation. The initial form and the mutant were represented in the second generation not in equal numbers, but there were considerably less mutants which has led to further elimination of mutants.

A comparison of the data on the compound population which was sown in Moscow in 1937 with those obtained in 1938 at the same place in Moscow (table) has shown that in 1938 the elimination of the mutant forms has considerably increased, i. e. the same result was obtained as in simple populations. In 1938 in the compound population the mutant *H. s.* var. *nonaristatum* was eliminated to 100%, which testifies to its low biological fitness. The

Locality and year of cultivation	*H. s. medicum* Körn. 046	*H. s.* var. *triaristatum* Kraj., awns on the spikelet glumae	*H. s.* var. *compactum* Kraj., dense eared	*H. s.* var. *Pismenkovi* Kraj., curved straw	*H. s.* var. *fistulosum* Kraj., tubular	*H. s.* var. *nonaristatum* Kraj., awnless	Mortality of 046 in %	Mortality of the mutants in %
Moscow, 1937	185 (200)	164 (200)	168 (200)	80 (150)	38 (50)	75 (100)	7.5	18.0
	196 (200)						2.0	16.0
	140 (150)						6.7	46.7
	46 (50)						8.0	24.0
	96 (100)						4.0	25.0
Odessa, 1937	196 (200)	182 (200)	118 (200)	63 (100)	30 (50)	60 (100)	2.0	4.0
	173 (200)						13.5	41.0
	81 (100)						19.0	47.0
	43 (50)						14.0	40.0
	79 (100)						21.0	40.0
Moscow, 1938	1861 (1990)	1010 (1190)	264 (672)	148 (560)	56 (261)	6 (221)	6.5	15.1
	1633 (1655)						1.4	60.8
	1213 (1293)						6.2	73.6
	796 (812)						2.0	74.8
	1087 (1108)						1.1	97.4
Odessa, 1937	90 (100)	105 (150)	119 (150)	115 (150)	—	40 (100)	10.0	30.0
	»						»	20.7
	»						»	23.4
	»						»	—
	»						»	60.0
Moscow, 1937	95 (100)	140 (150)	144 (150)	101 (150)	20 (40)	66 (100)	5.0	6.7
	»						»	4.0
	»						»	32.7
	»						»	50.0
	»						»	34.0
Moscow, 1938	2085 (2100)	1189 (1362)	595 (1008)	103 (370)	98 (297)	0 (67)	0.8	12.7
	»						»	41.0
	»						»	71.2
	»						»	67.1
	»						»	100.0

mutant *H. s.* var. *Pismenkovi* was eliminated to 71.2%, which similarly points to its low viability and biological fitness. The lowest percentage of elimination was shown by the mutant *H. s.* var. *triaristatum* (12.7%); this shows that this mutant is the most viable and biologically fitted one as compared with the others.

We do not dwell in detail on the analysis of the data obtained; it may be done by everyone who will study the table.

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EXPERIMENTAL MORPHOLOGY

ON THE LENS-FORMING ABILITY OF THE EYE OF ADULT AMPHIBIAE*

By V. V. POPOV

(Communicated by I. I. Schmalhausen, Member of the Academy, 23. VI. 1939)

The purpose of the present work was to repeat preceding experiments ([1–14]), but taking into consideration and eliminating their defects. Since our earlier experiments failed to yield any definite results, the task of my present study was practically the same: to solve the problem of the lens-forming properties of the definitive eye.

As hosts I used in these experiments adult *Bombina bombina* and *Rana temporaria*, and *Rana esculenta* which had not reached their full growth; as donors—embryos, young tadpoles, late tadpoles and adult individuals of the same species.

The operations were made on submerged animals after the hosts were preliminarily narcotized in ether vapours. The right eye was operated upon in every case, the left one was left as control.

For the extraction of the lens from the host's eye I made an incision in the cornea and dissected so far as possible the filaments of Zinn's zone. After this the lens was extracted together with its pouch. This operation presented no difficulties, especially in *Bombina*. The material intended for grafting was marked by means of disinfected carmine powder mainly in donors that survived. I will not dwell on every method of marking used by me, since I have described them in two earlier communications ([10],[11]). The graft itself was made in Ringer's solution with the help of finely sharpened pincers and of glass-needles with their ends rounded by melting. In some cases the eye lids of the animals were temporarily sutured for closing the wound.

The heads of the animals with marked grafts were fixed by a saturated sublimate solution with acetic acid and the sections stained with haemalaun, the rest of the material was fixed by Zenker's liquid and stained with boric carmine only.

Grafts of Unmarked Epidermis of Young Tadpoles. This series was arranged with the intention to throw light on certain moments of the transformation of the epidermis of young tadpoles into the lens. If such a transformation was found to be actually possible

* The results of the present research have been reported to the conference of the Chair of Histology and Embryology of the State University at Gorkij on October 11, 1938, and to the Department of Organogenesis of the Institute of Experimental Morphogenesis of the Moscow State University on December 22, 1938.

under the influence of the adult eye, then its individual phases could be followed by fixing the hosts in a series at short intervals soon after the operation. In such a series one could dispense with the marking of the implants which certainly is not indifferent for them.

The results of these experiments—a total of 23—proved fully positive, since I succeeded in observing different stages of the transformation of the implanted material into the lens in sections from it.

Grafts of Marked Epidermis of Young Tadpoles. While most animals of the preceding series were fixed on the days immediately following the operation, in the experiments of this series the fixation was accomplished usually not until 10—25 day after the beginning of the experiment.

The series includes 64 experiments. In a few cases, as this had been also observed in the preceding experiments, the lens did not appear. This should evidently be explained by the falling out of the implant. When the lens was present, disseminated particles of carmine were, as a rule, visible in it. The marked lenses, i. e. those undoubtedly originating from the implants, were in some cases quite well and regularly differentiated, but in many cases they differed from the lenses of the unoperated side by their noticeably smaller size. However, in isolated cases the size of the induced lenses approached the normal one.

It is of interest to note that the lenses obtained in our experiments, particularly those that had been fixed sufficiently late, were usually surrounded by a thin, but quite well expressed layer of connective tissue, to be short—by the lens capsula. My observations make me believe that the capsula of the lens is formed from the connective tissue of the vitreous humor. This origin is ascribed to it by the majority of the authors who studied its typical development. The capsula of the lens in my experiments was undoubtedly formed under the influence of the lens which had formed before it.

The form-building connexion between the lens and its capsula has been observed here for the first time, and it should be assumed that it is of general occurrence not only under the conditions of my experiment, but in the normal development of the eye as well.

In several cases I observed the appearance of isolated filaments of Zinn's zone, distributed quite regularly, i. e. extending from the capsula of the induced lens towards the membrana hyaloidea of the host's eye. It is quite possible that if the experiment was protracted long enough, Zinn's zone would reach or closely approach its complete development.

Main Conclusions and Prospects of Further Work

1. The eye of adult Batrachians possesses, like the eye of the embryo and that of the tadpole, an ability to induce lens-formation.

2. It induces the formation of the lens from bits of trunk epidermis of young tadpoles implanted into it, provided the typically formed lens has been preliminarily extracted.

3. The lens is actually formed from the implant and not from the eventually incompletely eliminated lens of the host. This follows from: a) the results showing the gradual transformation of the implant into a lens, b) the approximative agreement between the size of the implant and the respective lens, and c) the presence of the carmine particles, which was used in most of the experiments for marking the implants, in the lenses.

4. Lenses are not formed from bits of epidermis of late tadpoles, young animals of this year and of adult animals.

5. Embryonic epithelium, evidently because of the great difference in the age of donor and host, disintegrates in the eye of the adult animal and, consequently, is not transformed into a lens.

6. In several cases a certain discrepancy was observed between the histological differentiation of the induced lens and the formation of its general shape. However, in spite of the presensce of a strongly loosened, fibrous mass, constituted by twisted lens-fibres of irregular shape, these lenses, being defective as to their external morphological differentiation, could be regarded as such only conventionally.

7. Around the lens formed in the experiment, one observes sometimes the appearance of a connective tissue lens capsula and in a number of cases even of isolated filaments of Zinn's zone.

8. The eye of the adult animal induces the formation of a lens only in the case of integrity of the former. Bits of retina implanted under the trunk epithelium of embryos do not induce the formation of the lens from this epithelium.

It would be of interest to reproduce our experiments on mammals, and in case they will prove successful, to attempt to transfer them for purely practical purposes to human patients.

Experiments of this kind may, possibly, bring us nearer to the substitution of lenses, extracted on account of cataract. At present we are starting our experiment on mammals.

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PALEONTOLOGY

REPRESENTATIVES OF *OCHOTONIDAE* (*DUPLICIDENTATA*, *MAMMALIA*) IN THE PLIOCENE OF THE USSR

By A. I. ARGYROPULO and I. G. PIDOPLICHKA

(Communicated by A. A. Borissiak, Member of the Academy, 2. VII. 1939)

The relationship between numerous species and genera of *Lagomorpha* as treated in literature, particularly among members of the family *Ochotonidae*, is still rather vague, and in a way very intricate. This is largely due to the lack of summaries [after the appearance of works by F. Major (1), and partly by Viret (2)], most of the decriptions of new forms being superficial and non-critical.

In the present paper we make an attempt to clear and classify the available material on *Ochotonidae* from the Late Tertiary, mainly from the Pliocene of the southern regions of the European part of the USSR. Some data have been published on Pliocene species of *Ochotonidae* from certain regions of South-Eastern Europe and Eastern Asia (China and Mongolia). More numerous are publications on Quaternary finds of *Ochotonidae* in the same regions, which in most cases have already been presented by remains of modern species.

Ochotona (Proochotona) gigas sp. n.

Material. Nos. 4936, 4937, 4972. Complete or somewhat damaged lower jaws, materials of the Odessa Paleontological Expedition, collected by T. G. Gritzai. Catalogue numbers of the same expedition. Preservation of bones fair, bone strongly mineralized, sonorous, of yellowish-brownish and brown colour. Nos. 3093, 3593, 3787, 3793 from Bessarabia (Pileney Moldovan), collected by I. P. Khomenko, 1915. Bone whitish-yellow, dark and brown in colour, strongly mineralized.

Horizon and Locality. Odessa «Catacombs», brownish-red clay, filling cracks and karstic interstices in Pontian limestone, referred to the Middle Pliocene. Pileney Moldovan of Bessarabia—sand and gravel deposits referred by Khomenko to the Middle Pliocene.

Description. A very large species, equal in size but to the Chinese Quaternary *O. complicidens* Boule et Teilhard (see below). Alveolar length of molars of the lower series 11.3—12.6 mm. Length—breadth of P_4 2.6—3 mm, greatest height of jaw 28.6—29 mm, the same behind the molars 10.9—11.1 mm, thickness through symphysis mentalis 4.3—4.5 mm. Breadth of processus angularis (see below) 18.5 mm, height of jaw from the anterior (lower) angle of the angular process to the proc. coronoideus 19.6—20 mm. P_3 identical in structure to P_3 in *O. eximia* and recent species of the genus (Fig. 1). The lower jaw differs from that in *O. eximia* not only in size, but in many structural characters (Fig. 2). Condyloid process directed relatively more backwards with a somewhat expanded summit which causes the incisura semilunaris posterior to be far deeper than in *O. eximia*. The posterior edge and upper angle of the processus angularis lies above the alveolar level of molars.

Ochotona (Proochotona) eximia Chomenko

Material. Complete or somewhat damaged lower jaws Nos. 4938, 4939, 4941 (dextrae), 4920, 4921, 4927, 4928 (sinistrae) and more than 10 other jaws from Odessa (T. G. Gritzai's collections), over 20 lower jaws from Bessarabia (collected by Khomenko, 1915), a fragment of a lower jaw from the village Taraklia (Bessarabia), type of Khomenko. Paleontological Museum of the Odessa University.

Horizon and Localities. Materials from T. G. Gritzai's collections found in brownish-red clays filling karstic interstices and cracks in Pontian limestones of Odessa. These clays belong to the Middle Pliocene. Materials from collections of Prof. Khomenko derived from sand and gravel deposits of Bessarabia (Pileney Moldovan, Kafritza, Khadji-Abdul, Karbolia) assigned by him to the Middle Pliocene; a fragment of a lower jaw from Taraklia was found in Maeotic deposits referring to the Late Miocene.

On this species we had an opportunity, in addition to the original description by Khomenko (3), to study likewise the type and the new and abundant material quoted above. The conclusions reached by us are somewhat different from those of Khomenko. In the description of *Proochotona* it is quite correctly emphasized that importance the structure of the first premolar of the series (P_3) has for the identification of fossil pikas. After the recent works by Viret (1929), Teilhard de Chardin (1930—31), Young (1931) the above comes still more to show. On the other hand, the pattern of this tooth in recent species of *Ochotona* is very constant, notwithstanding the abundance of species. Thus, the essential differences in the structure of P_3 in *Ochotonidae* under description may in a number of cases serve as one of the basic generic (or sub-generic) characters.

While describing *Proochotona*, Khomenko, using F. Major's summary and conclusions from his work, has marked the close relation of the pika described by him to *Lagopsis* (however, this genus has still retained roots on the molars). Indeed, the general structure of P_3 in *Proochotona* corresponds to the plan characteristic of *Lagopsis*, distinguished from the latter only by the lack of the second deep T-shaped fold on the inner side of the crown. Furthermore, Khomenko states that from the recent *Ochotona* the genus described by him differs in the unpaired lobe in the anterior portion of P_3 (comparison was made by him not on the basis of the material, but after figures from works of various authors). However, this point which served to differentiate the *Proochotona* is not correct, as shall be seen later.

The third premolar of the lower jaw in all modern *Ochotona* has the following pattern (Fig. 1). The general outline of the crown is that of a truncated triangle, its base facing the next premolar of the series. Its apex is separated from the main portion by two deep narrow re-entrant folds and forms an unpaired lobe of varying shape. In young specimens this lobe usually lies below the main portion of the tooth and is often separated from it by an enamel rim which wears away with age. Sometimes the edges of the lobe are undulate. On the outer side in the main portion of the tooth another deep re-entrant fold is observable (Fig. 1).

An identical structure is exhibited by P_3 in *Proochotona*, and even though varying somewhat in details follows the same line of development. Khomenko's statement that in *Ochotona* «the anterior part of P_3 is devoid of the unpaired lobe» is puzzling indeed, though the isolation of *O. eximia* into a separate genus is based on this character alone. Apparently, this is exactly the character which distinguished *O. eximia* as a representative of the genuine *Ochotona*.

According to the latest data of Young (4) and Schlosser (5), *Ochotona* have been known in Asia from the Middle Miocene, whence up to the present three fossil forms have been described. A brief account of their characters is given below.

Ochotona gobiensis Young (1931) is known from the Middle Miocene (beds with remains of *Platybelodon* in the Tung-Gur basin near Irdin Mancha) of Mongolia. *O. gobiensis* is a relatively large species (length of *P—M* inf. 10.5 mm). In structure P_3 differs sharply both from the recent *Ochotona* and from piping hares of the *O. eximia* Chom. group. The outer side of this molar displays but one deep re-entrant fold, the anterior one being barely marked as a small depression on the edge of the elongated lobe. Thus, the structure of the molar under description is more simplified than in *O. eximia*.

Ochotona lagreli Schlosser (1924) is known from the Pontian stage Ertemte, Mongolia[5]. This species is of about the same size as *O. gobiensis* (length of *P*—*M*—11 mm). Construction of P_3 conforms to the plan characteristic of *O. eximia* and of recent species. The differences are rather slight and manifested in the larger size of the posterior region of this tooth as against the reduced area of the anterior lobe. The inner re-entrant fold is small and runs nearly longitudinally along the long axis of the tooth.

«*Ochotonoides*» *complicidens* Boule et Teilhard[6] (1928)—known from several localities of Shansi, Shensi and Hansu (China), where its remains have been found in red clay and lower strata of loess. Their age has been determined as Upper Pliocene or Lower Quaternary. *O. complicidens* is the biggest among the common *Ochotonidae*, since its lower tooth row is 12.3 mm in length, the maximum length of skull —75 mm. P_3 (2.8 mm in length) is similar in structure to *O. eximia*, except for its anterior unpaired lobe having notched edges, in shape usually recalling that of a trefoil; the notch on the outer side of this lobe is particularly deep. *O. complicidens* is isolated by Teilhard and Young[7] into a separate genus *Ochotonoides* (1931) mainly on the basis of craniological characters. The latter show no deviation from the plan of their specific divergence within the genus *Ochotona*, and the name *Ochotonoides* is to be included in the generic synonymy of *Ochotona*. The possibility is, however, not excluded of applying this name to designate intrageneric groupings (see below, also cf. «USSR Fauna«, *Duplicidentata*, A. I. Argyropulo).

Having analyzed our material, we suggest the following diagnosis for *O. eximia* Khomenko (1914). *O. eximia* is a larger species than the known recent representatives of the genus. The length of the series of lower molars (alveoli) is 9—11 mm. Length—breadth of P_3 from 2—2.3 to 1.9—2 mm. Length of the lower jaw (angular) up to 39 mm, height (maximum) 24.8 mm, the same behind the tooth row—9.4 mm. Thickness of the jaw through symphysis mentalis 3.6—3.9 mm. Breadth of angular process from the apex of the angle in the lower region of dentale 14.7 mm, height of the jaw from last point to the coronoid process 17.5 mm. Maximum length of the lower series of molars in the largest recent *Ochotona* (*O. alpina alpina* Pall.) is equal to 9.4 mm, length of jaw 37.8 mm, greatest height behind the molars 6.2 mm. Third lower premolar (P_3) in *O. eximia* is arranged entirely after the fashion of those in recent *Ochotonidae* (Fig. 1). Lower jaw (Fig. 2) in comparison to living species is massive and shortened, with a relatively very broad angular process. Condyloid process straight, little expanded if at all in the upper portion and incisura semilunaris posterior with a very slanting, nearly straight upper border. Posterior angle and upper border of processus angularis lie below the level, less frequently on the level of the alveoli of the last molars.

Ochotona eximia is known from the Upper Miocene of Eastern Rumania (Taraklia), Middle Pliocene of the south of the USSR (Odessa) and, probably, from the Lower Quaternary (or Upper Pliocene) of Western Siberia (Ishim and Selim Dzevar) as well. The material from the above-mentioned places preserved in the Paleontological Institute of the Academy of Sciences of the USSR is very abundant (8), but unfortunately so much damaged and fragmentary that no precise determination is possible. The length of alveoli of the lower series of molars in these piping hares ranges from 10 to 13.5 mm, the height of the jaw behind *MM* being 7.8—10.1 mm. These variations in size are evidently exceeding individual variation of *O. eximia* (to judge from our material), and it is possible that in Western Siberia, as well as in the European part of the USSR had lived more than one species of *O.* gr. *eximia* (see below).

Ochotona antiqua Pidoplitshka

Besides the described large Tertiary pikas from the Upper Pliocene of the southern part of the Odessa province, Moldavian ASSR and Bessarabia, are known small pikas which have been referred by us in 1938 to *Ochotona pusilla antiqua* subsp. n. (I. G. Pidoplichka, Materials for the Study of

the Fossil Fauna of the Ukrainian SSR, Fasc. 1, 1938, p. 124). The analysis of the material available on this form has enabled us to isolate it as a species of pikas from the Upper Tertiary, closely related to those of the living species from the *O. pusilla* group. A brief description of this form follows.

Material. Complete or somewhat damaged lower jaws from the Odessa province, Moldavian ASSR and Bessarabia. Nos. 2617, 3804, 3806, 3798 (dextrae), 2616, 2618 (sinistrae) and more than 50 other lower jaws from the same collections.

Their types are No. 2616 subadultus from the village Novopetrovka, Grossulovo district, Odessa province, and No. 2618 adultus, from Greben-

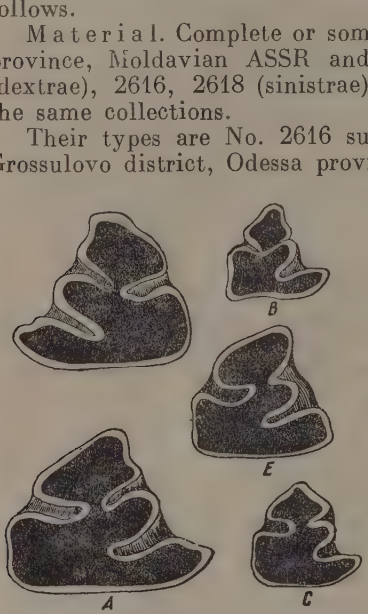

Fig. 1. P_3 (inf.). *Ochotona*: *A*—*O. gigas* sp. n. (adult.), *B*—*O. pricei* Thos. (subadult.), *E*—*O. eximia* Chom. (senilis), *C*—*O. alpina* Pall. (adult.).

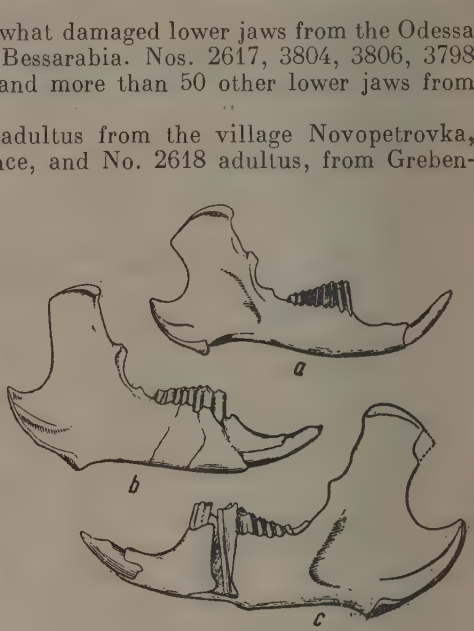

Fig. 2. Mand. inf.: *a*—*Ochotona alpina alpina* Pall., *b*—*O. eximia* Chom. (No. 4938), *c*—*O. gigas* sp. n. (No. 4919).

niki of Moldavian ASSR, collections of I. G. Pidoplichka, 1934, bearing numbers according to the catalogue of the Zoological Museum of the Academy of Sciences of the Ukrainian SSR.

Horizon and Localities. Upper part of sand and gravel deposits of the Kuchurgan stage (upper part of the so-called Balta series) of Late Pliocene age: Grebenniki of Moldavian ASSR, Grossulovo, Mikhailovka, Trostyanetz, Novopetrovka (Savitzkaya), Andriashevka of the Odessa province, and of Middle Pliocene (?) age—Pileney Moldovan, Kafritza in Bessarabia (from collections of Chomenko, 1915).

Diagnosis. *Ochotona antiqua* is a more diminutive species than *O. eximia*, in size somewhat exceeding (sometimes equivalent to) the modern species *O. pusilla*. Length of the series of lower molars (alveoli) 7.8—9.8 mm. Length and breadth of P_3 equal to 1.3—1.8 mm, angular length of lower jaw 25.5—27.6 mm, greatest (condylar) height of lower jaw 16—19.6 mm, the same behind the tooth row (M_3) 5.3—7.2 mm, thickness through symphysis mentalis 2.3—2.8 mm, breadth and dorsoventral measurement of incisor 1.3—1.6 mm.

According to structural and morphological peculiarities, a considerable part of lower jaws in *O. antiqua* recalls such in *O. eximia*, i. e. by being more inflated as compared to pikas from the *O. pusilla* group.

The relationship between all the species investigated by us (*O. gigas*, *O. eximia*, *O. antiqua*) and *O. ursui* described by Simionescu(9) from the

Pliocene of Rumania (Malusteni) is vague. According to the first original description, *O. ursui* is a diminutive species with the lower series of molars measuring up to 8 mm in length, i. e. not exceeding in size some of the recent species of *Ochotona* and much inferior in this respect to *O. eximia*. In its second work on Beresti vertebrates from the Pliocene, Simionescu determines as *O. ursui* a still larger pika with the lower series of molars measuring 11 mm in length and lower jaw between M_1 and M_2 up to 9 mm in height. Obviously, *O. ursui* Simionescu is to be considered as a synonym of *O. eximia* (cf. «Pliocene fauna of the Kuchurgan district and adjoining localities» by I.G. Pidoplichka, manuscript).

Indications as to the occurrence of *Myolagus meyeri=Prolagus meyeri* Tschudi (Kontkevich, 1887) within the limits of the Ukrainian SSR have not been borne out by evidence. Reference to the occurrence of the same species in the Kuchurgan deposits (Lungerhausen, C. R. Acad. Sci. URSS, 1934, No. 6) applies to *O. antiqua*, and most probably Kontkevich, too, had found *Ochotona* rather than *Prolagus*.

On the basis of the data enumerated above, the fossil Tertiary pikas of the USSR may be divided into two groups: the first group—*O. eximia*, and the second group—*O. antiqua*. The former, including *O. gigas* and *O. eximia*, by their larger size, general robustness of the lower jaw, large angular process, differ sharply from recent species of *Ochotona*, constituting an extinct group. Inasmuch as no complete skulls of European Pliocene pikas have been so far known, we are provisorily leaving the entire group under the name designated by Khomenko (*Proochotona*) considering it, however, as subgeneric only.

The second group is closely allied to the living pikas and equivalent to them in size. The pikas from the Upper Pliocene *O. antiqua* may be directly linked onto the Quaternary members of the *O. pusilla* group, this fact having been established upon the finds of remains of fossil pikas in Lower, Middle and Upper Quaternary deposits of the southern parts of the Ukrainian SSR (I. G. Pidoplichka, report at the First Paleontological Conference in Moscow, 1938).

Thus, the development of the group of pikas of the genus *Ochotona* in the south of USSR proceeded from larger Upper Tertiary to more diminutive fossil Quaternary and contemporary ones.

The genus *Ochotona* in our concept falls into 3 or 4 subgenera: one or two fossil ones, i. e. *Proochotona* and, perhaps, *Ochotonoides* too, and two recent ones: *Ochotona* s. str. (synonym of *Pica*, *Ogotoma*, *Lagomys*, *Conothoa*, *Abra*) and *Tibetholagus* Argyropulo (subg. n. in litt.) The last subgenus has been established for *O. koslovi* Buchner on the basis of craniological characters, sharply separating this species from a number of others.

The history of representatives of *Ochotonidae* in the Asiatic continent and in Eastern Europe is still unclear. Asia is now the chief habitat of numerous representatives of the genus *Ochotona*. Their remains are abundant, as we see, also in the Pliocene of Asia. The genus *Ochotona* was known to exist almost unaltered even in the Miocene of Mongolia (*O. gobiensis*). It is noteworthy that almost all fossil representatives of *Ochotona* were distinguished by larger size. Earlier finds in Asia are still very scarce, affording no opportunity for tracing the origin of the modern genus *Ochotona*. The Oligocene Mongolian *Desmatolagus* Matth. et Gr. still had the dental formula of hares: its molars, as far as part of the species were concerned, were probably deprived of roots. The Upper Oligocene *Agispelagus* Argyropulo (in litt.) from Middle Asia had a dental formula identical with *Ochotona*, while it exhibited, like *Titanomys*, a number of primitive characters; it should, apparently, be considered as an extinct side branch of a family which had but indirectly

participated in the formation of the modern *Ochotona*. All the facts described in this communication are believed by us to contribute to an exhaustive account of the fossil Tertiary *Ochotonidae* of Eastern Europe and Asia.

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ERRATA

Vol. XXIII, № 2, article by A. A. Kuzmenko, p. 192, lines 6 and 12 from above: for 10—14-hour read 10—14-day.

Vol. XXIII, № 2, article by A. I. Korenyako, title and throughout the article: for microbacteria read mycobacteria.

Vol. XXIII, № 4, articles by V. G. Alexandrov and O. G. Alexandrova, p. 384, line 10 from below and p. 388, title: for achenes read caryopsis.

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